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16. Abstracts: The objective was to study methods of sampling for mercury in gas streams containing high SO_2 concentrations. The ultimate objective was to develop a sampling procedure adaptable to copper-zinc smelters as well as fossil-fuel fired plants. Gold forms a strong amalgam with mercury resulting in its use here to quantitatively adsorb mercury from a gas stream. Mercury amalgamation accompanied by a flameless atomic absorption mercury procedure was utilized. The collection procedure consists of modifying a standard EPA isokinetic sampling train, utilizing two modified impingers containing 10 grams of gold chips to collect the mercury vapor as an amalgam. Particulates containing mercury are collected on a fiber glass filter upstream of the gold amalgam. The analytical procedure consists of transferring the modified impinger containing the mercury amalgam to an induction furnace. The induction field instantaneously volatilizes the mercury and an air stream carries it through a quartz optical cell positioned in the 254 mμ mercury line of an atomic absorption spectrophotometer. The mercury concentration is calculated from a peak obtained on the strip chart recording of the absorption pattern. Accurate results are obtainable from stack gases within two days of on-site sampling.

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THE DEVELOPMENT OF THE GOLD AMALGAMATION SAMPLING AND ANALYTICAL PROCEDURE FOR INVESTIGATION OF MERCURY IN STACK GASES

by

G. William Kalb

and

Charles Baldeck

for

The ENVIRONMENTAL PROTECTION AGENCY

Contract Number 68-02-0341

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INTRODUCTION

Limited investigations of mercury concentrations in coal have shown a national range of 0.05 to 0.50 ppm with some regionalized exceptions.[1,2,3,4,5] This mercury, naturally occurring in coals, is volatilized during combustion of the coal in fossil-fuel fired steam generating plants. The present consumption of coal could result in the release of a significant quantity of mercury to the atmosphere.

The mercury volatilized during the combustion stage is not entirely lost to the atmosphere. During the gas cooling stages in generating plants, involving the economizer, air preheater, cyclones, considerable ductwork, and the stack, volatilized mercury appears to condense onto the flyash. This conclusion, based on a few limited studies,[6,7,8] shows that an average of 10% of the original mercury is recovered in the flyash with undetectable amounts present in the bottom ash. Because mercury is not observed in the bottom ash it is assumed that all the mercury is volatilized and the flyash concentrations result from recondensation. This theoretical conclusion has shown that we cannot directly extrapolate coal concentrations to atmospheric releases. To understand the behavior of mercury in stack gases it is necessary to determine a mass balance, showing the amount of mercury in the original coal and the resultant concentrations in the bottom ash, fly ash and stack gases. This requires an analytical method by which we can reliably measure mercury in stack gas concentrations.

Present methods for determining mercury concentrations in stack gases are

wet scrubber sampling trains using acidic-oxidizing solutions to absorb the volatile mercury from the gas stream. The adaptability of solution sampling trains to mercury stack gas sampling is dependent upon the ability of the solution to oxidize elemental mercury to the +2 valence state thus removing it from the gas stream as it bubbles through the solution. Acidic permanganate and/or iodine monochloride solutions have been utilized by the Environmental Protection Agency, TVA and TraDet. The reactions and oxidation potentials are shown in Table 1. As can be observed from the oxidation potentials, SO_2 from the stack gases will reduce both the MnO_4^- and ICl. Because of this, excess permanganate and iodine monochloride must be used and a constantly decreasing concentration of oxidant will be observed.

Table 1. Reactions and oxidation potentials.

$SO_2 + 2H_2O \rightleftharpoons SO_4^= + 4H^+ +$	$2e^-$				-0.17
$2Hg \rightleftharpoons 2Hg^{++} +$	$4e^-$				-0.92
$Cl^- + \frac{1}{2}I_2 \rightleftharpoons ICl_{aq.} +$	e^-				-1.19
$Mn^{++} + 2H_2O \rightleftharpoons MnO_2 + 4H^+ +$	$2e^-$				-1.23
$Mn^{++} + 4H_2O \rightleftharpoons MnO_4^- + 8H^+ +$	$5e^-$				-1.51

Deterioration of the oxidant has been observed with both acid $KMnO_4$ and ICl sampling trains during sampling. In addition, acidic $KMnO_4$ undergoes autodecomposition. After a representative sample is obtained in the sampling train the mercury concentration is determined by reducing the excess oxidant and the mercury, and aerating the solution, carrying the

mercury through an inclosed quartz tube in an atomic absorption spectrophotometer. Hydroxylamine hydrochloride and stannous chloride are used to reduce the acidic $KMnO_4$ samples and hydroxylamine sulfate is used to reduce the ICl samples.

Because of the potential condensation of mercury in the fly ash it is desirable to simultaneously collect a particulate sample. This requires the use of an isokinetic sampling train for an extended sampling period. Because of this and the requirement that an extended sampling period is required for a representative sample it is desirable to have at least a ½ hour sampling period. Because of the SO_2 concentrations in the gas stream this is not feasible with wet oxidizing solution trains.

It is the objective of this investigation to study other methods of sampling for mercury in gas streams containing high SO_2 concentrations. The ultimate achievement of this study is to develop a sampling procedure adaptable to copper-zinc smelters as well as fossil-fuel fired plants. Smelters roast sulfide ores in a partially reducing environment releasing large quantities of SO_2 which may or may not be recovered in an acid plant. The SO_2 concentrations may exceed 6% in these plants.

Silver and gold amalgamation reactions with mercury chemically favor the complete recovery of mercury in a gas stream. Silver reacts with SO_2 forming a sulfide surface layer (common tarnish) eliminating its application to stack gases. One of several possible reactions for this would be:

$$SO_2 + 6Ag \longrightarrow Ag_2S + 2Ag_2O$$

In addition gold forms a strong amalgam with mercury resulting in the use of it in this study to quantitatively adsorb mercury from a gas stream.

Mercury amalgamation accompanied by a flameless atomic absorption mercury procedure is utilized in this investigation.

ANALYTICAL PARAMETERS

Gold amalgamation has been used as a concentration and interference elimination step in the flameless atomic absorption procedure for determining mercury in water, fish, coal, etc.. The digested sample is reduced and the elemental mercury is aerated onto the gold foil, where it forms a stable amalgam. Since other compounds which would absorb at the mercury resonance wavelength of 254 mμ are not collected onto the gold, they are vented from the system during the amalgamation step. The amalgam is then fired in an induction furnace, revolatilizing the mercury which is carried by an air stream through a quartz cell in the optical path of an atomic absorption spectrophotometer. The instantaneous heating of the gold in the induction field produces a very rapid release of mercury from the gold and a sharp peak is obtained on the recorder readout of the spectrophotometer with the peak height proportional to the mercury concentration.

In the modification of this procedure for stack gas analyses, the amalgam is obtained by passing the gas through a quantity of gold supported in a tube (called an amalgamator) placed in a standard EPA sampling train. When sufficient gas has been drawn through the amalgamator, it is placed in the induction furnace and fired as described above. A schematic diagram of the analytical apparatus utilized in this procedure is shown in Figure 1. Immediately after analyzing the amalgam obtained from the sampling train, standards are run on the same amalgamator by placing aliquots of a standard mercury solution in the aeration cell shown in the figure. A 100 or 200 ppb

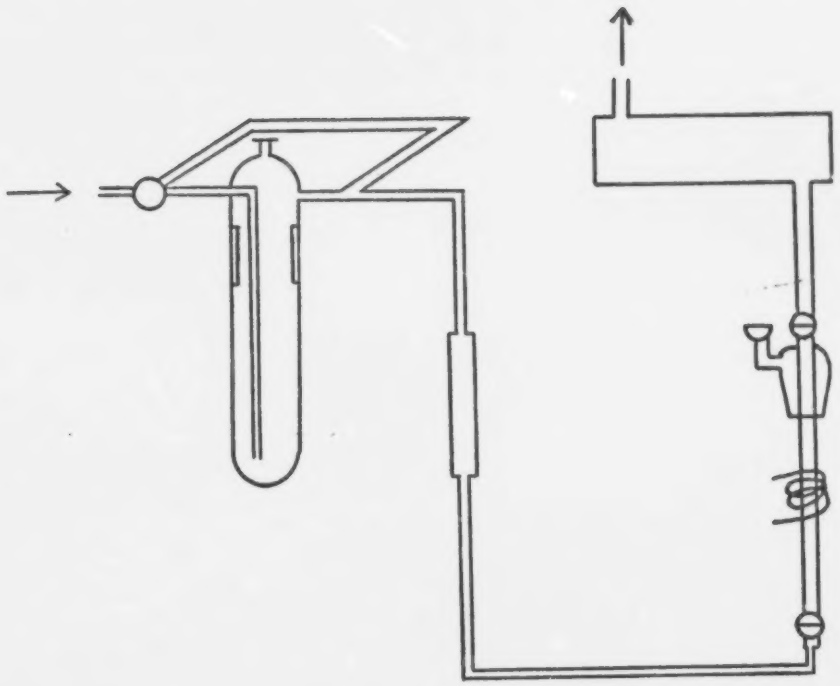


Figure 1. Schematic Diagram of the Analytical Apparatus

mercury standard is prepared fresh daily from a 1 ppm stock solution. The stock and working standard solutions are fixed with 5% concentrated nitric acid to retard deterioration. The 1 ppm stock solution is prepared weekly from a 1000 ppm stock mercury solution prepared from mercuric chloride and containing 5% concentrated nitric acid. After the standard is placed in the aeration cell it is reduced by the addition of 1 ml. of 20% $SnCl_2$ in 50% HCl with a syringe inserted through the septum cover. The $SnCl_2$ reduces the oxidized mercury to elemental mercury which is readily volatilized by an air stream that is bubbled through the solution. The volatilized mercury is carried by the air stream through the gold foil where it is amalgamated. The amalgam prepared in this manner from standards is then fired in the same manner as the sample collected in the gas stream. Negligible blanks are obtained during the running of standards and since there are no chemicals used in the sampling procedure the stack samples do not have a background level requiring a blank determination. This is a major advantage over the present wet chemical sampling trains.

There are several parameters that must be optimized in the analytical procedure. The parameters studied in this investigation include:

(1) design of the amalgamator,

(2) absorption cell design,

(3) amount and type of gold,

(4) the shape and peak height of the absorption curve as a function of the firing temperature of the amalgam,

(5) the air flow rate for aerating the standard solutions and for transporting the volatilized mercury from the amalgamator to the quartz cell. The air flow rates are given in the units used on the Perkin-Elmer atomic absorption spectrophotometer flowmeter: for conversion to ml/min. refer to Appendix II.

1- Design of the Amalgamator

The optimized amalgamator designed to support from 5 to 20 grams of gold is illustrated in Figure 2. It is adaptable to both the standard EPA isokinetic sampling train and the induction furnace. This design permits inserting the amalgamator into the sampling train in place of an impinger during gas sampling and then inserting it into the induction furnace for firing the amalgam. This eliminates both (1) the necessity of having to modify the existing standard sampling train and (2) repacking the gold amalgam in a different holder for firing in the induction furnace. Two amalgamators were investigated; (1) a 15 mm design, shown in the illustration, and (2) a 25 mm design containing a 25 mm bulge about 1½" high where the gold is located, and a perforated glass plate to support the gold. The large amalgamator effectively decreases the flow rate of the gas stream through the supported gold. This decreased flow rate was found to be unnecessary under the conditions investigated. The large amalgamator was found to heat unevenly in the induction field producing irregularly shaped peaks. In addition, local overheating of the gold would result in fusing some of the gold chips together and the amalgamator would break from thermal stress around the perforated plate. In order to obtain reasonably symmetrical peaks using the large amalgamator a rather low flow rate (to minimize turbulence of the air flow through the perforations in the plate) and a low firing temperature (to avoid fusing the gold and breaking the glass) were necessary. At low flow rates, slight random variations in the flow can cause a comparatively large variation in sensitivity, especially with large samples (see Figures 10, 11, 12). This makes it undesirable to work at

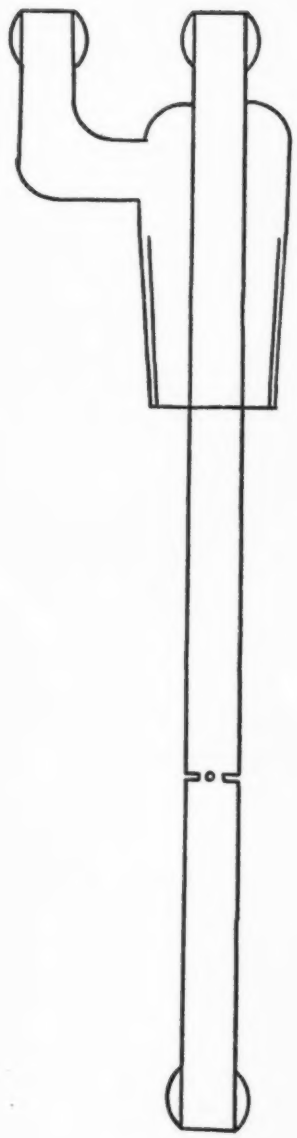


Figure 2. Illustration of the 15 mm Amalgamator

the low flow rates, and was one of the reasons why the large amalgamator was rejected in favor of the straight type.

Both the illustrated three finger support for the gold and a perforated plate support were investigated. The perforated plate, when rigidly affixed to the sides of the tube, tends to break with extensive sudden heating in the induction field. Additional problems were observed with the flow patterns developed by the disk. The three finger support did not experience this extensive breakage. When the three finger support is used, a 2 gram gold wire plug supports the gold foil chips. The optimized amalgamator was constructed of pyrex. Quartz would be a better construction material but the cost for four ground glass quartz joints or one joint and a graded seal becomes more expensive than the breakage. The 15 mm three finger pyrex amalgamators have been used extensively (several hundred firings) without breakage but they do show glass strain when investigated optically. Additional study may show that a sintered glass support would be acceptable. This has not been investigated at this time.

2- Absorption cell design

Three absorption cells were designed as illustrated in Figure 3. The first two cells were 6½" and 3" long with quartz endplates. The third cell was ½" wide with two quartz windows. The first two cells are high volume peak height cells ie. more and more mercury enters the cell during firing, reaching a maximum concentration (peak height on recorder strip chart) corresponding to measuring all the mercury at once. The third cell approximates an integrating cell, theoretically measuring each increment

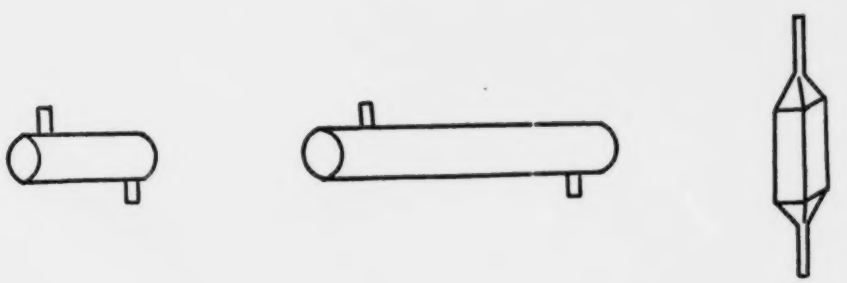


Figure 3. Illustration of the 3 Absorption Cells

of mercury concentration as it passes through the cell. An ideal peak height cell theoretically measures all the mercury at one time, which would, if a large enough cell were used, result in a plateau at the greatest absorption corresponding to the time involved before the cell starts eluting itself. The small cell measures concentration as a function of time, which is extremely dependent on all the above parameters including the exact alignment of the amalgamator in the induction furnace. It does not have a sufficient volume to average out small non-uniformities in the release of mercury, and the curves obtained with it show doublets, triplets and pre-peaks, Due to the impossibility of maintaining all of these parameters constant, this cell is not suitable for peak height measurement. Instead the curve should be integrated which requires a recorder and a spectrophotometer which reads out in absorbance. The integrating cell does decrease sensitivity considerably, permitting determinations to be made at higher mercury levels ie. longer stack sampling periods. Since the available instrumentation was not suitable for integration of the peaks obtained with the ½ inch cell, the 3 inch peak height cell was utilized in most of the studies. This limited the amount of mercury that could be measured in the linear section of the analytical curve (approximately 2.0 μg.).

3- Amount and Type of Gold

Compressed gold wire and gold chips, both 0.007" thick were studied. The gold chips, between 1/8" and 1/16" square, packed more evenly in the amalgamator resulting in a more uniform temperature in the induction field, giving better reproducibility. Ten grams of gold chips were found to be

sufficient in all the sampling studies. In tests with standards of up to 10 μg. of mercury, 10 grams of gold quantitatively removed the mercury from the air stream without leakage, which, at the observed stack concentrations, is sufficient for one hour runs.

4- The shape and peak height of the absorption curve as a function of the firing temperature of the amalgam

Because the temperature achieved by the gold is induced, it is extremely difficult to measure. Thermocouples, etc., are self inducing in the induction field and optical pyrometers are only usable at the higher temperatures. Because of this the percent variac setting of the induction furnace is recorded instead of the temperature. The temperatures obtained in the induction field are a function of the density of packing of the gold, the amount of gold, the cross-sectional area of the gold in the amalgamator, and the air flow rate through the amalgamator. In order to eliminate any variations in heating due to individual differences in the amalgamators, the firing temperature studies for each absorption cell length were performed using one amalgamator with the standard packing: a 2.00 gram gold wire plug supporting 10.00 grams of gold chips. In order to examine the relationship between air flow and firing temperature the study was performed at several air flow rates. This was done for each of the absorption cells investigated. Figure 4 shows the typical effect on peak shape as the firing temperature is varied at both the high and low flow settings, for the 3 inch cell. Similar results are observed with the 6½inch cell. When the ½ inch cell is used, the combination of the low sensitivity (large concentration of mercury required to be on scale) and the short path length causes pre-peaks or

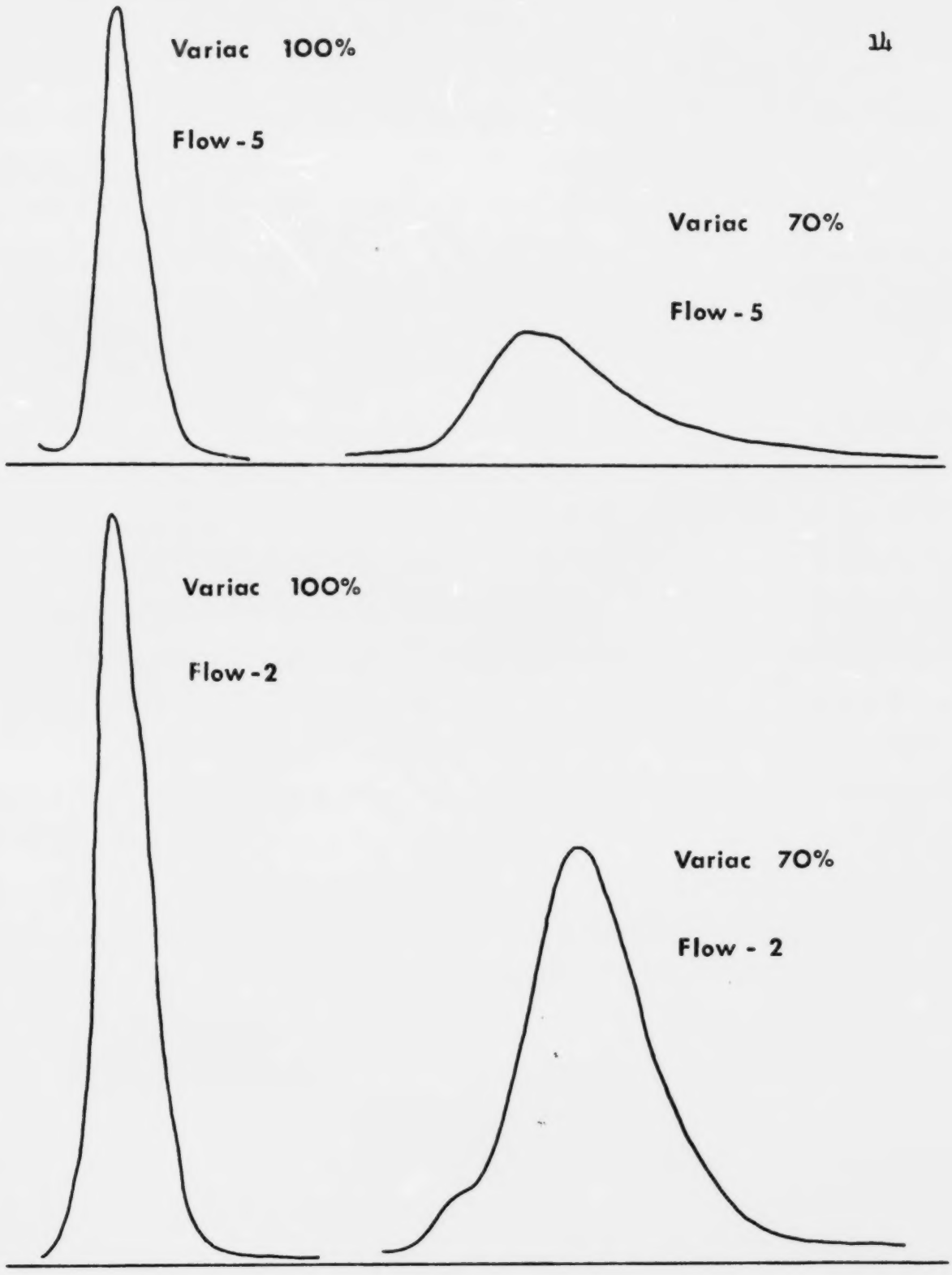


Figure 4. Peak Shape as a Function of Firing Temperature and Flow Rate

doublets to appear, limiting the usefullness of this cell with the present instrumentation. At low firing temperatures, the pre-peak is higher than the main peak; as the firing temperature is raised the main peak becomes higher. Figure 5 shows typical peaks obtained with the ½ inch cell as the firing temperature is varied.

In general, either a decrease in firing temperature or an increase in air flow rate makes the peak lower and broader. The combination of high air flow rate and low firing temperature results in the peaks tending to trail. The change in peak height observed as the firing temperature is varied at several flow rates is summarized in Figures 6, 7, 8 and 9. In general, the optimum combination of firing temperature and air flow rate is one that gives a symmetrical Gaussian peak with no doublets or pre-peaks, representing a uniform release of the mercury from the amalgam during firing. This was achieved over a fairly wide range when either the 6½ inch or the 3 inch cell was used. The best setting for the firing temperature is one at which the gold just starts to glow at the end of the firing period. This permits a visual check of the degree of firing, but is sufficiently low to eliminate fusing of the gold. Firing temperatures are not a critical parameter with the longer cells as long as they are high enough to volatilize all the mercury and avoid excessive trailing of the peaks. A wide range of temperatures were observed to release the mercury; the lower settings require a longer period of firing. The completeness of mercury volatilization is observable on the strip chart recording. With the standard 15 mm amalgamator containing 10 grams of gold chips and a 2 gram gold wire plug settings of 80 - 100% were utilized. Firing temperature can be used advantageously for

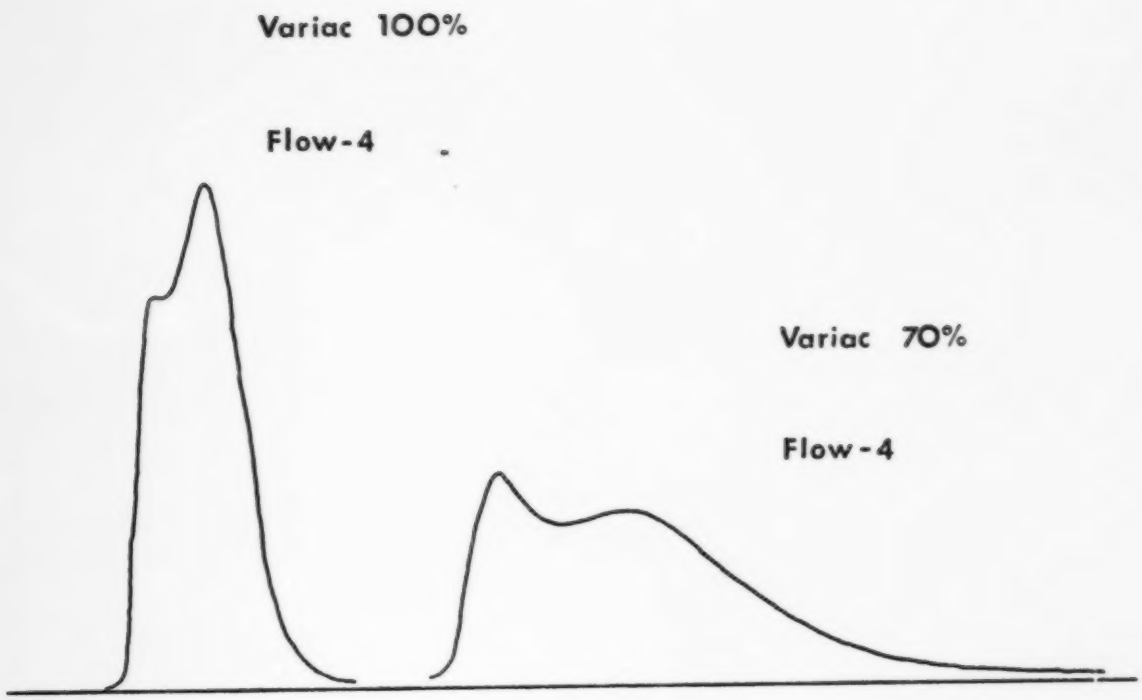


Figure 5. Peak Shapes obtained with the ½" Cell

15 mm Amalgamator

6 1/2" Cell

0.25 µg Hg

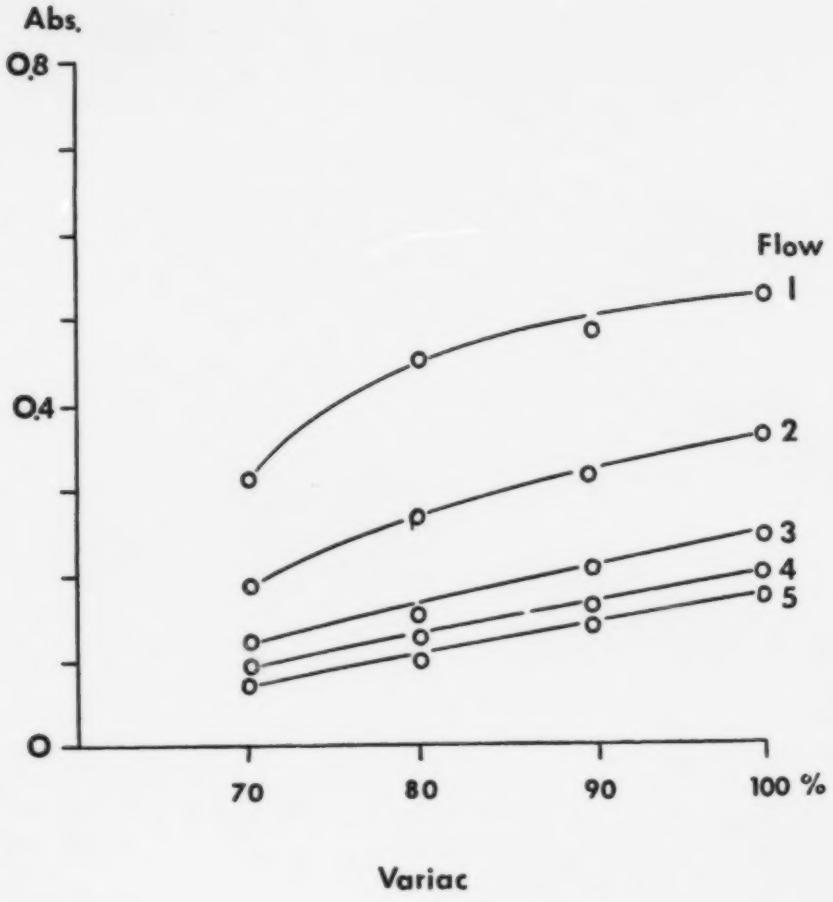


Figure 6. Peak Height as a Function of Firing Temperature and Air Flow Rate (15 mm Amalgamator, 6½" Cell)

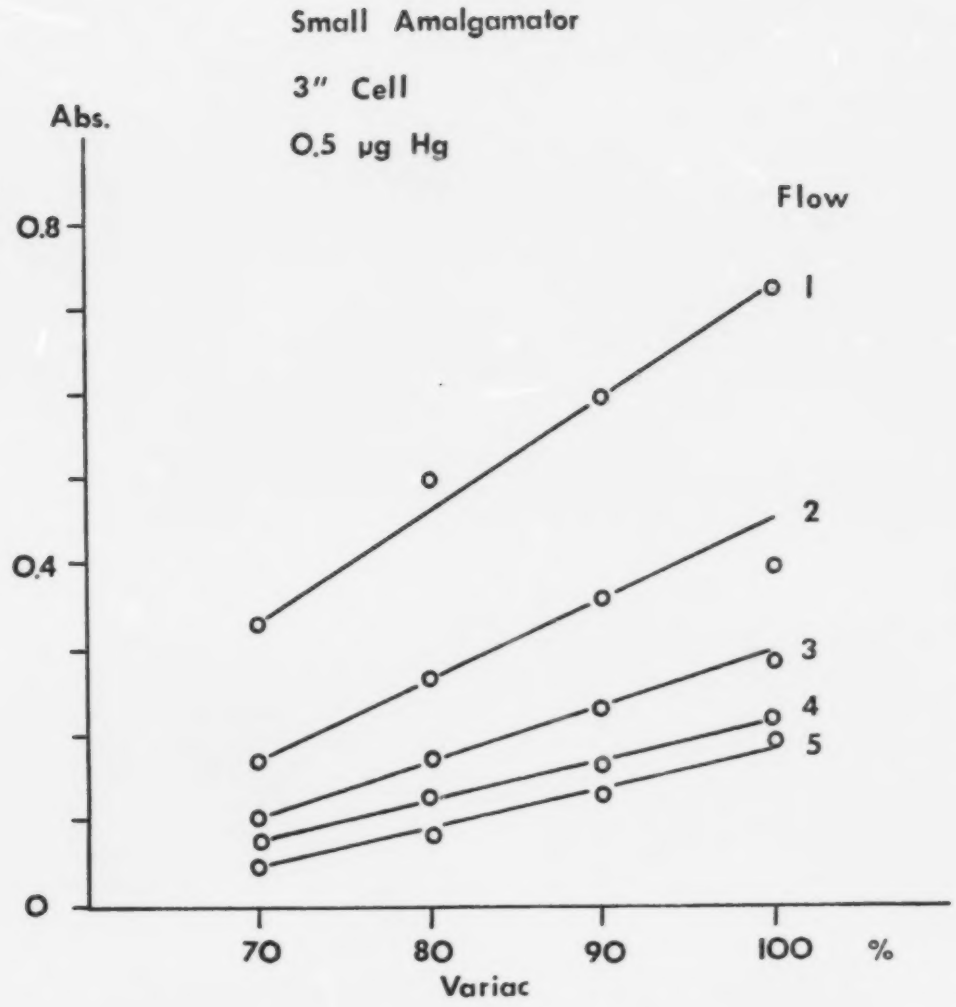


Figure 7. Peak Height as a Function of Firing Temperature and Air Flow Rate (15 mm Amalgamator, 3" Cell)

Large Amalgamator

3" Cell

0.5 µg Hg

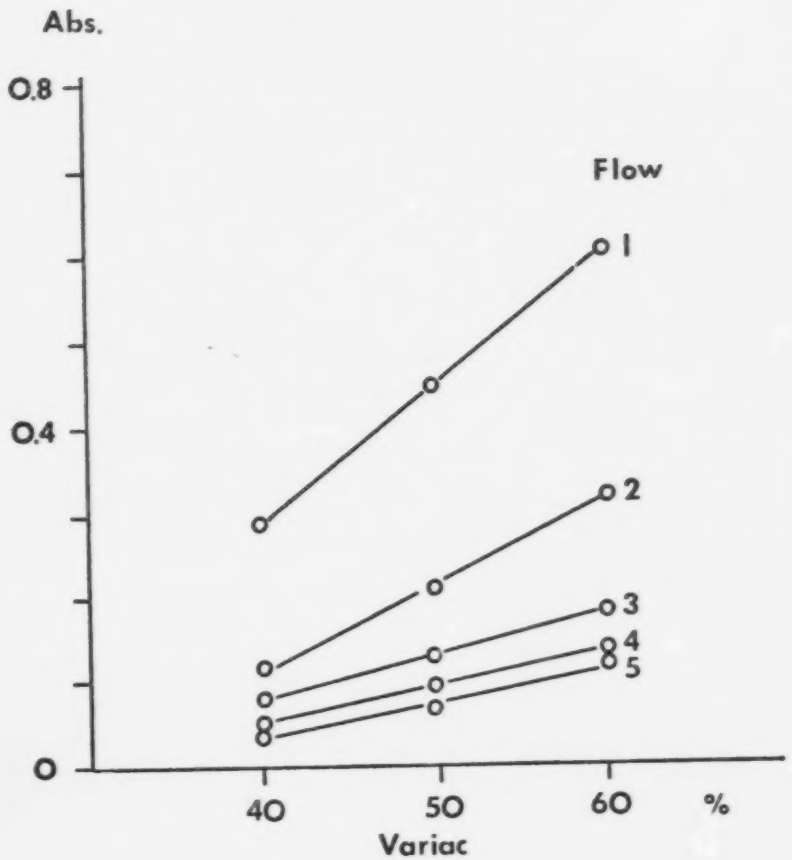


Figure 8. Peak Height as a Function of Firing Temperature and Air Flow Rate (25 mm Amalgamator, 3" Cell)

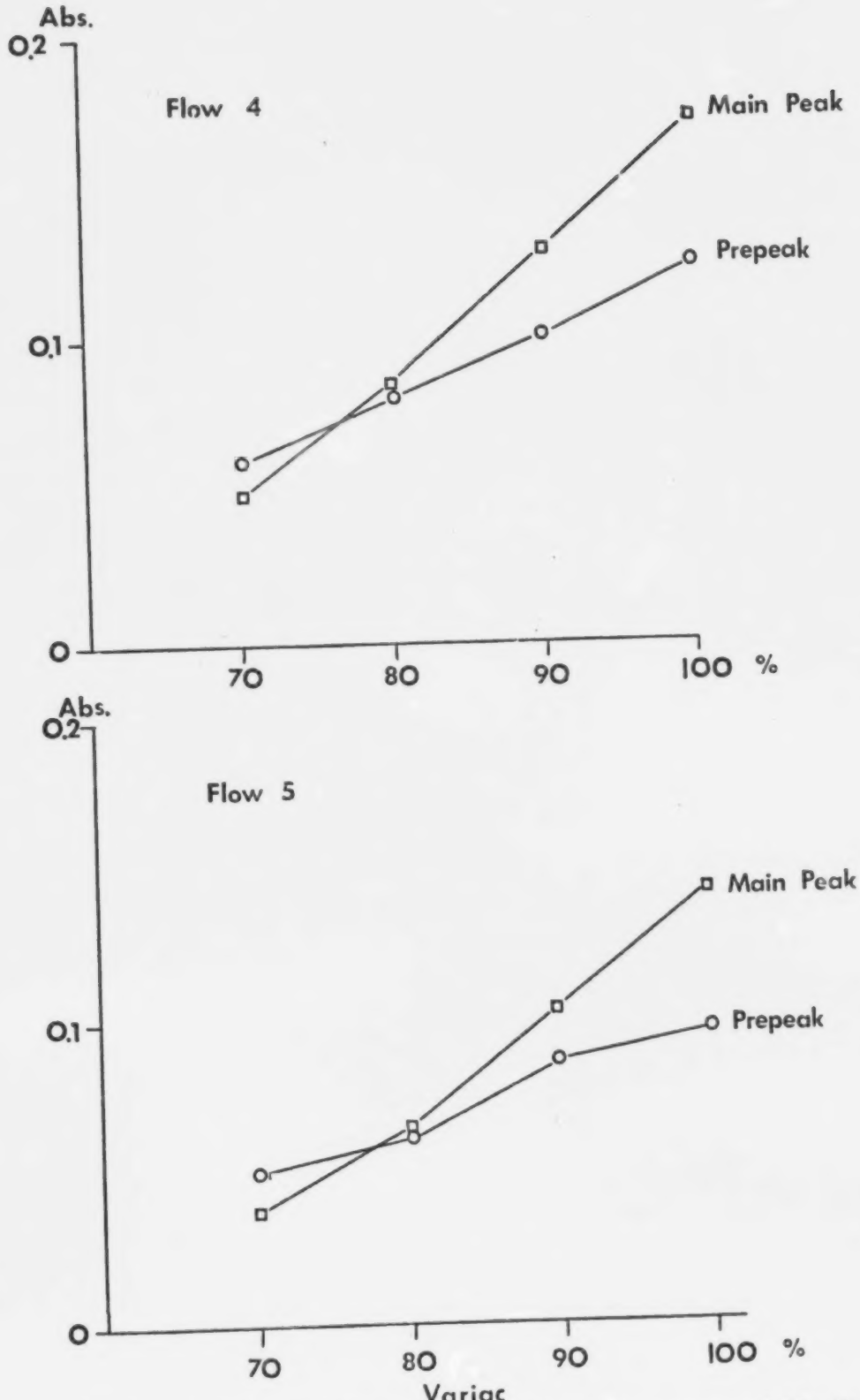


Figure 9. Peak Height as a Function of Firing Temperature and Air Flow Rate (15 mm Amalgamator, ½" Cell)

slight adjustment of sensitivity.

5- Air Flow Rate

For ease of operation and the manual reproducibility of settings it is advantageous to utilize the same air flow rate for aerating the standard solutions and carrying the revolatilized mercury from the amalgam through the quartz absorption cell. Slower flow rates just increase the aeration time required to volatilize the mercury from the standard solution, permitting us to optimize the air flow rate solely as a function of the sensitivity and peak shape observed from the absorption of the mercury at the 254 mμ line in the quartz cell. The time required for complete aeration of the standard solution at a given air flow rate was determined by volatilizing the mercury from the standard solution directly through the quartz absorption cell in the spectrophotometer (bypassing the amalgamation step). Figure 10 shows typical curves obtained and illustrates the dependence of complete volatilization on aeration rate. These curves were utilized to determine how long to aerate the standards at the selected flow rate. A summary of required aeration times for various flow rates is given in Table 2 and shows that complete aeration is a function of flow and time and nearly independent of sample size.

Table 2. Minutes of aeration required at various flow rates

Air Flow / Cell (Sample)	1	2	3	4	5
6½" (0.5μg)	12	5	3	2.5	2.5
3" (1.0μg)	12	5	3	3	2.5
½" (10.0μg)	12	6	4	4	3
3" (1.0μg) (lg. amalgamator)	12	-	-	-	2.5

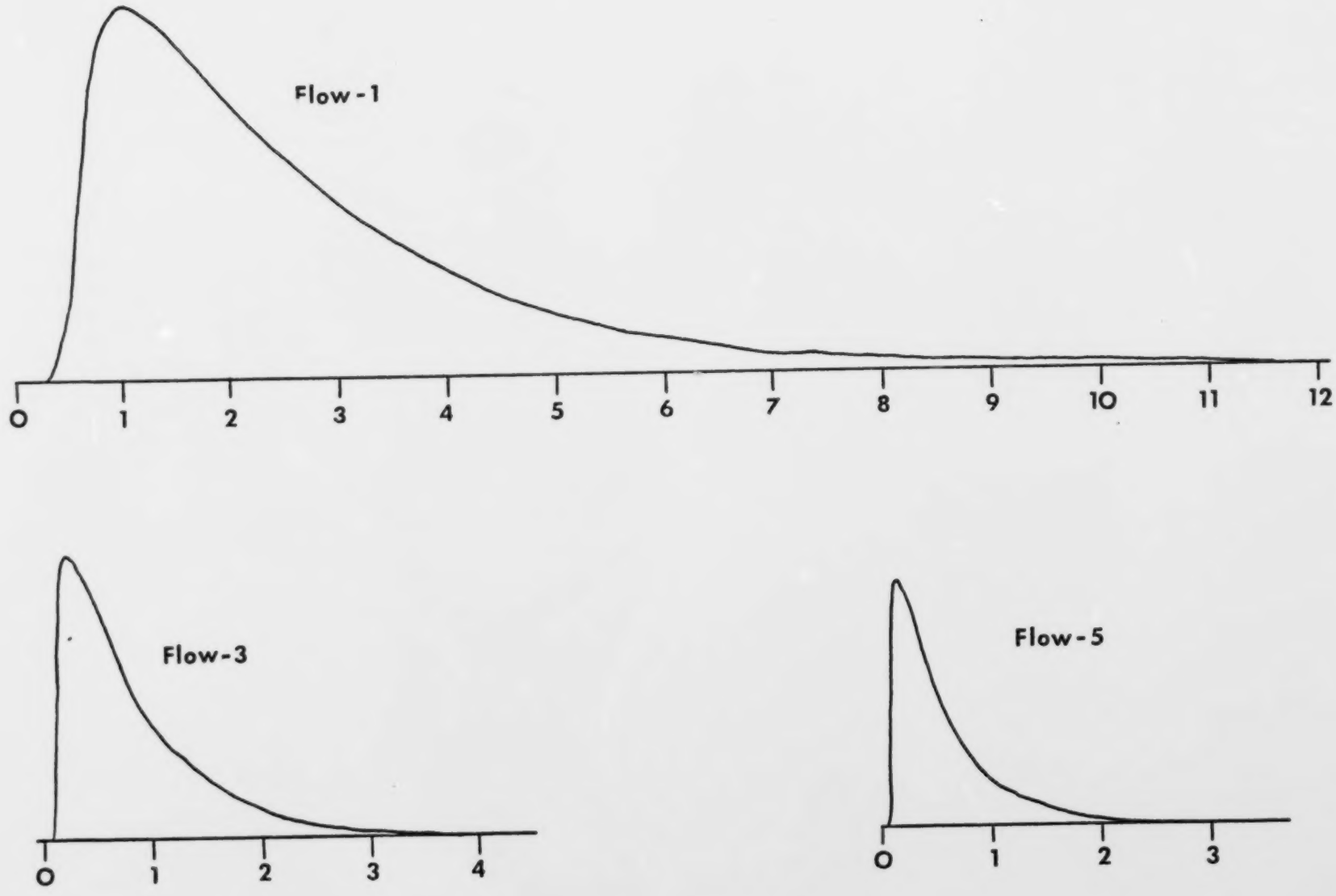


Figure 10. Illustration of Procedure used to determine Aeration Time of Standard Solutions

The dependence of peak height, or absorbance, on air flow rate was studied as a function of mercury concentration for each of the cells. The results are shown in Figures 11, 12, and 13. The slower flow rates greatly increase the sensitivity, and the effect is more pronounced with the shorter cells and higher mercury concentrations. (Some caution should be exercised when aerating the more concentrated standard solutions at the higher flow rates to insure that there is no bypass during the first few seconds of aeration, when the mercury concentration passing over the gold is very high.) This can be avoided by only partially opening the bypass valve on the aeration cell for the first 30 seconds. In effect, this aerates the highest concentration of mercury at a slower rate. This will slightly alter the shapes of the curves shown in Figure 10, increasing the total aeration time by 30 seconds. Air flow utilized for the majority of the standards and samples analyzed in this study was a total of 3½ minutes aeration time (30 seconds slow, 3 minutes at the full flow) at an air flow setting of 3 (1.4 liters/min.) with the white plastic ball on the Perkin-Elmer gas control regulator.

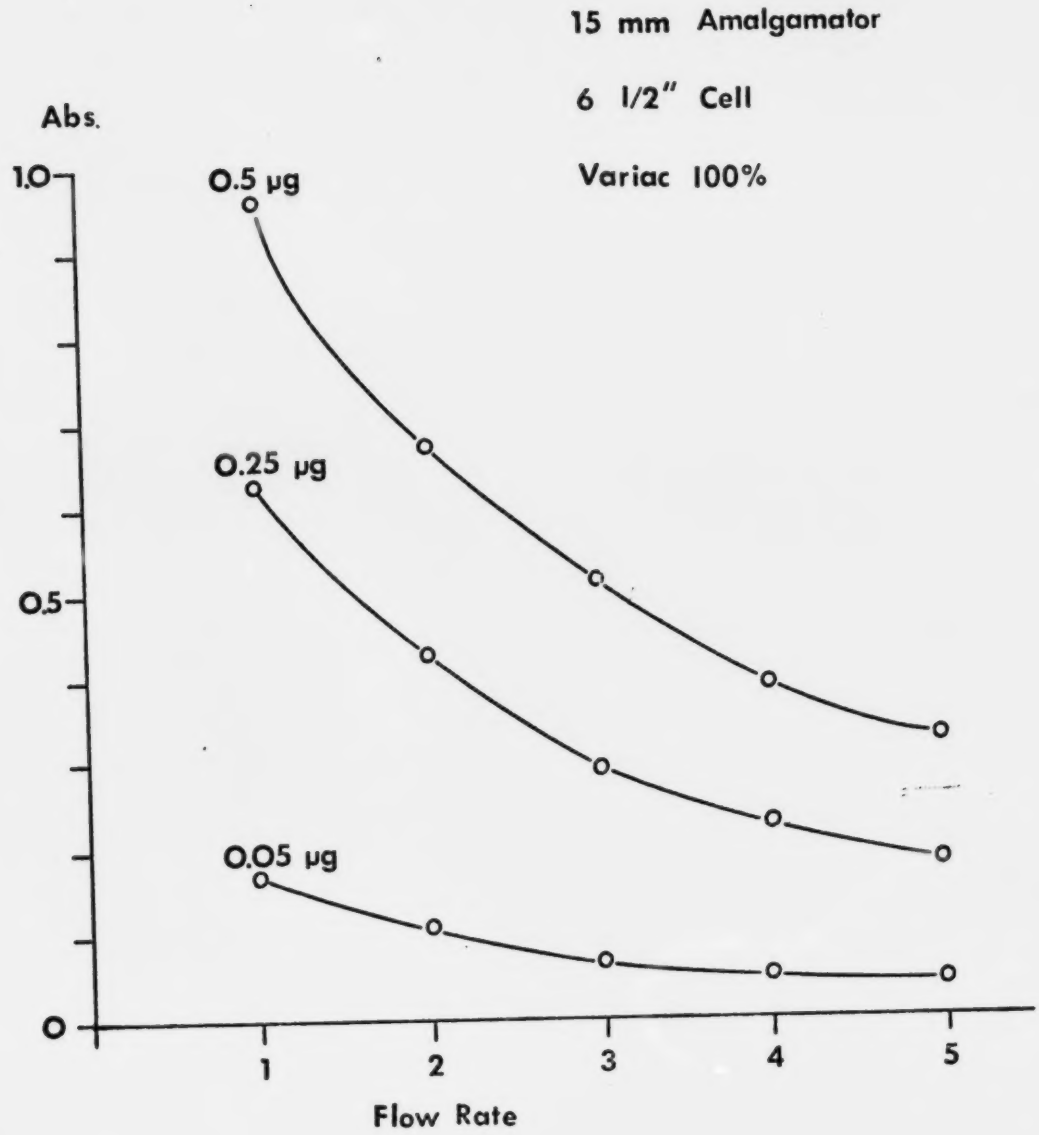


Figure 11. Peak Height as a Function of Flow Rate and Sample Size (15 mm Amalgamator, 6½" Cell)

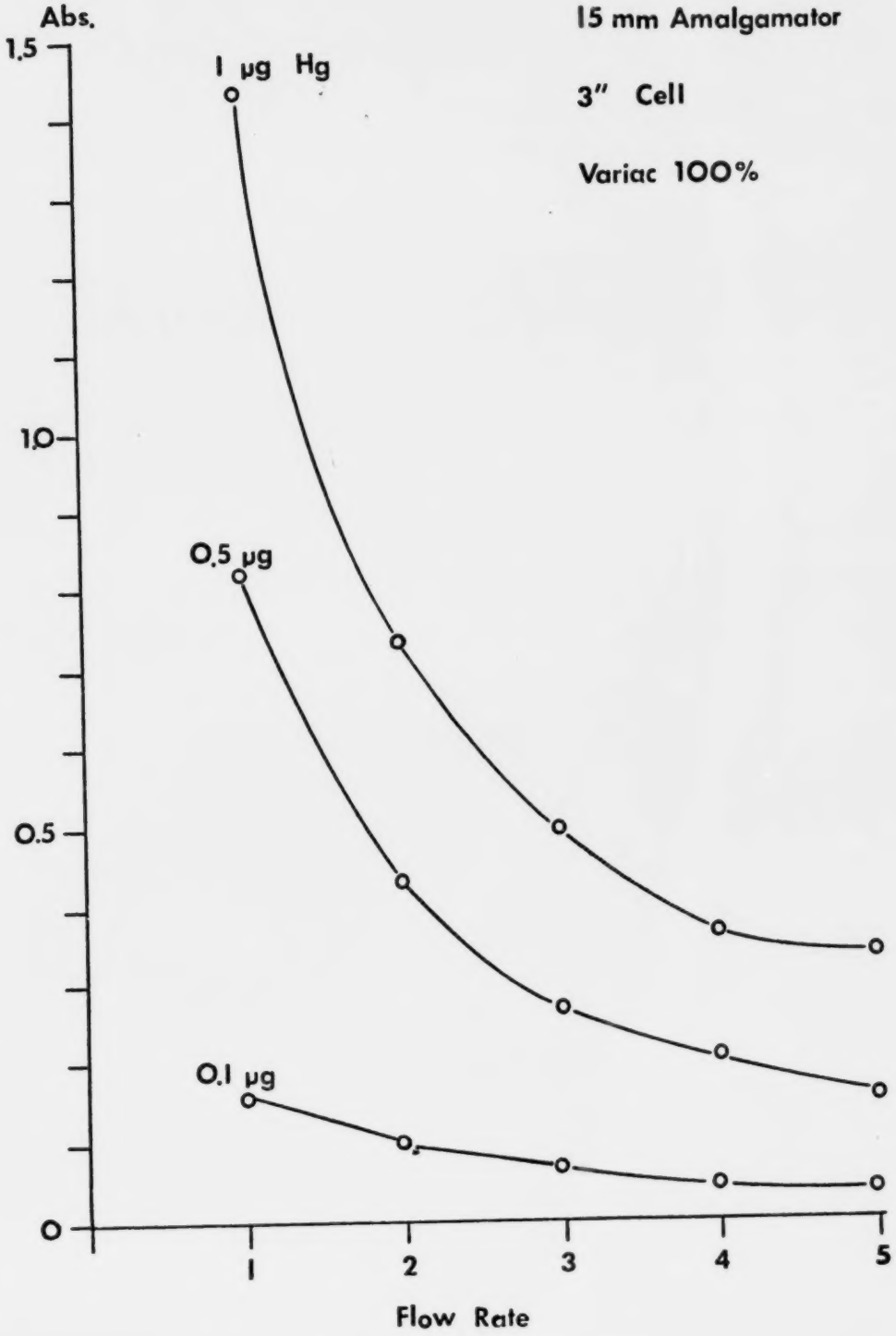


Figure 12. Peak Height as a Function of Flow Rate and Sample Size (15 mm Amalgamator, 3" Cell)

15 mm Amalgamator

1/2" Cell

Variac 100%

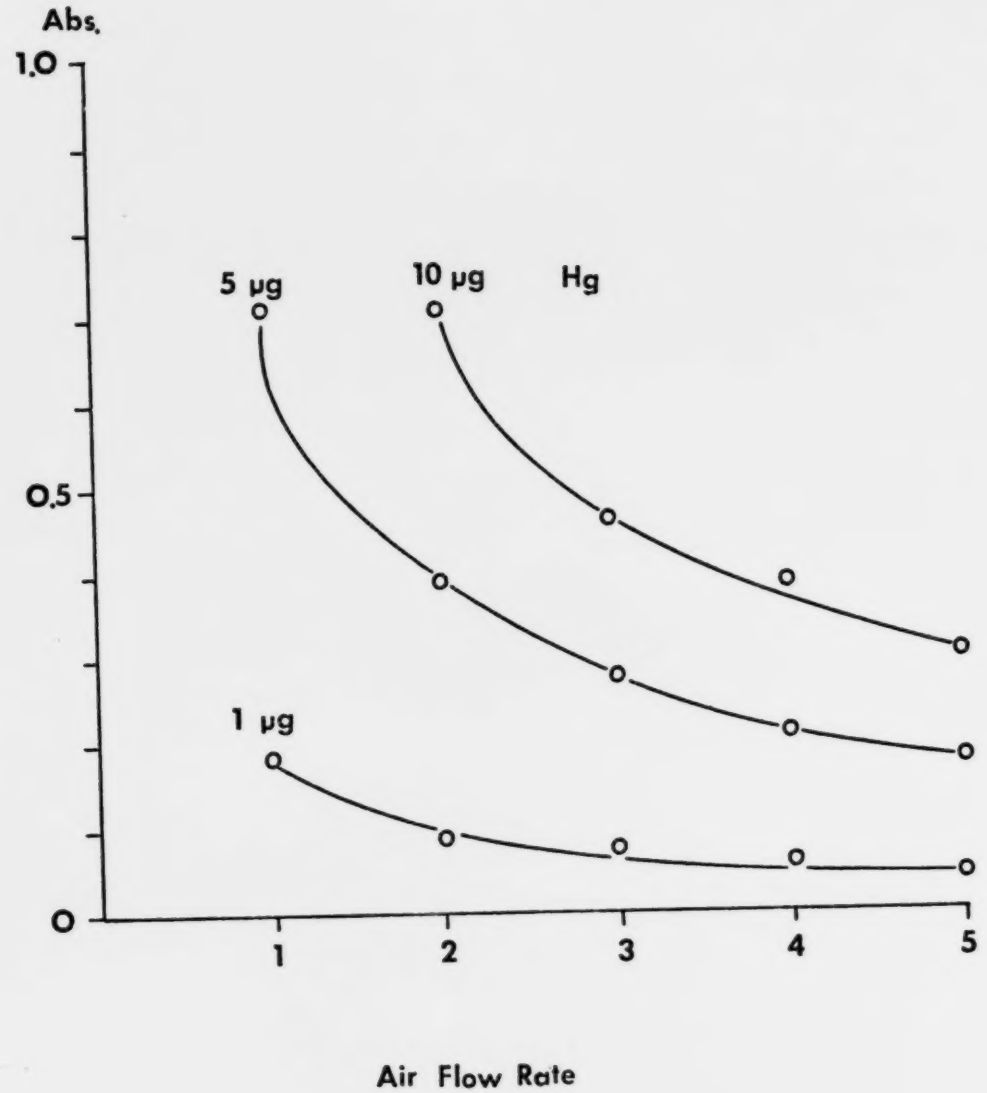


Figure 13. Peak Height as a Function of Flow Rate and Sample Size (15 mm Amalgamator, ½" Cell)

ANALYTICAL PROCEDURE

The studies optimizing the analytical determination of mercury resulted in the following settings and analytical procedure:

Atomic Absorption Spectrophotometer, Perkin Elmer Model 303

Mercury line	254 mμ
Noise suppression	1
Scale expansion	1
Lamp setting	(as prescribed)
Chart speed	60 mm.min. (during analyses)

Induction Furnace, Leco Model 521

Variac setting	80 - 100%
Grid	High

Amalgamator

15 mm dia. with three finger support

2 gram gold wire plug

10 grams of 0.007" thick gold chips

Air Flow

1.4 liters/minute

Aeration Time

3½ min. @ approx. 0.5 liters/minute

3 min. @ 1.4 liters/minute

The solutions and standards used in this study were prepared as follows;

Stock Hg solution, 1000 ppm in 5% HNO_3*

Prepared by weighing out 1.3535 g. of reagent grade $HgCl_2$, adding it to a 1000 ml volumetric flask containing 50 ml of conc. HNO_3 and diluting with distilled water.

Stock Hg solution, 1 ppm (prepared weekly)

Prepared by taking 1.00 ml of the 1000 ppm stock Hg solution, adding it to a 1000 ml volumetric flask containing 50 ml of conc. HNO_3 and diluting with distilled water.

Working Hg solution, 100 ppb (prepared daily)

Prepared by taking 50 ml of the 1 ppm stock Hg solution, adding it to a 500 ml volumetric flask containing 25 ml conc. HNO_3 and diluting with distilled water.

$SnCl_2$ solution, 20% in 50% HCl

Dissolve 100 grams of $SnCl_2 \cdot 2H_2O$ in 250 ml of conc. HCl (12M). Dilute to 500 ml with distilled water. Add a few pieces of metallic tin to the solution. This solution may have a cloudy appearance when first prepared; this does not affect its use.

In the optimized procedure, the straight amalgamator containing the stack sample is placed in the induction furnace; the top and bottom ball joints are connected so that the system is sealed with a constant air flow rate through the amalgamator into the quartz absorption cell. The gold is aligned in the furnace so that the tube is concentric with the induction coil and then fired at about 90%. The resulting peak appears on the recorder within a few seconds. A standard, approximating the observed peak, is

*ASTM, Mercury in Coal Methodology Group has tentatively proposed that all mercury standards be made up to contain 5% HNO_3 as a preservative. The 1000 ppm stock solution prepared in this way is stable for at least a year.

placed in the aerator and reduced with 1 ml of 20% $SnCl_2$ in 50% HCl, introduced by means of a syringe through the septum cover. A sufficient time, at least 1½ to 2 minutes, is allowed to assure that the gold has cooled to approximately room temperature since the last firing. The standard is then aerated for three minutes, (at an air flow of 3` amalgamating the volatilized mercury onto the gold foil. The amalgam is then fired at the same variac and air flow settings as the sample, producing a standard peak. Experience has shown that the standard more exactly reproduces the peak shape of the stack sample if the standard is aerated onto the top of the gold. This duplicates the direction of gas flow through the amalgamator during the sampling operation and places the bulk of the mercury onto the top layer of gold, promoting uniform release of mercury from both standard and sample.

Figures 14 and 15 show typical working curves obtained using the straight amalgamator and the 6½ and 3 inch cells respectively. The 6½ inch cell was useful up to about 2.0 µg of mercury. Figure 16 shows a typical working curve obtained using the large (25mm) amalgamator in conjunction with the 3 inch cell.

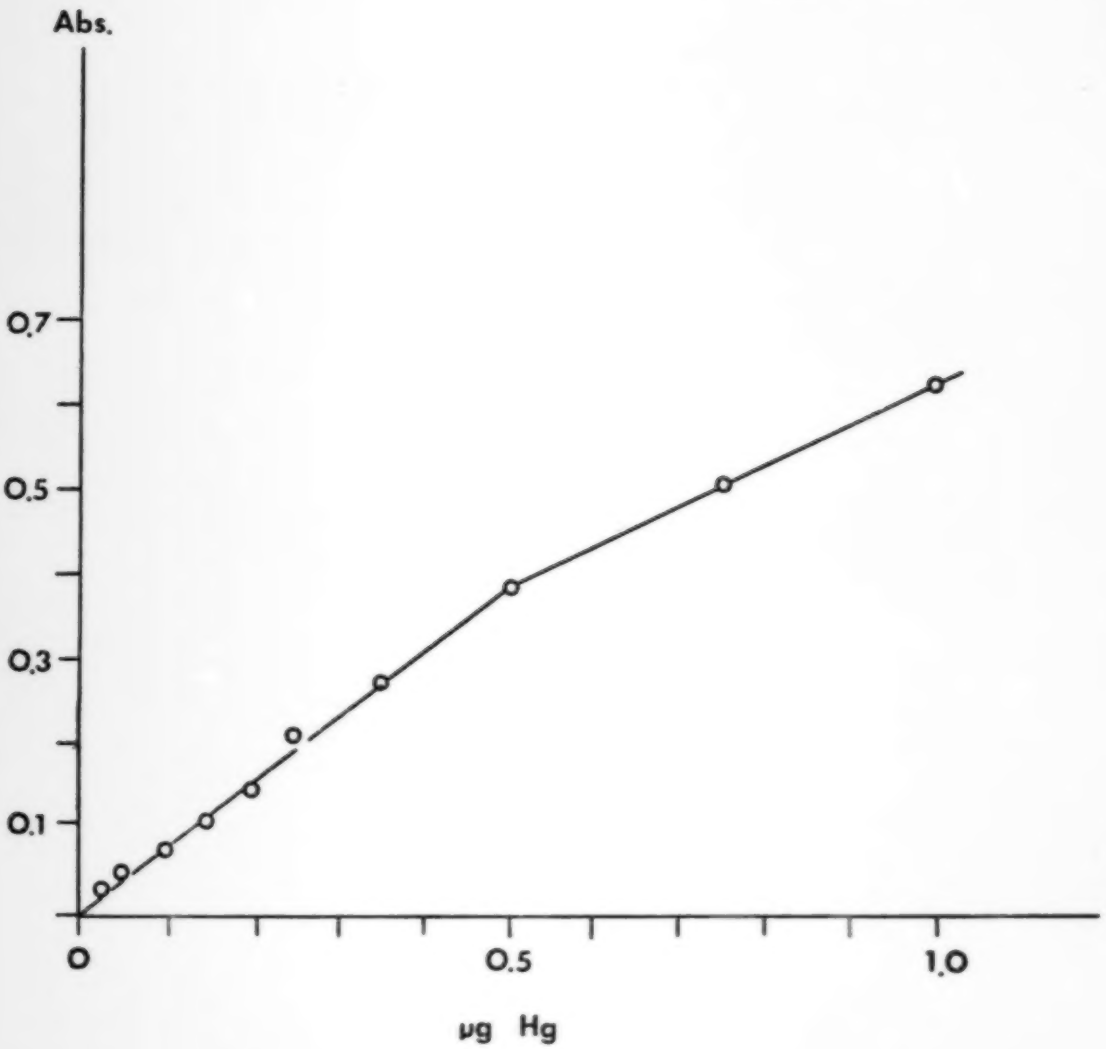


Figure 14. Analytical Curve obtained with 6½" Cell and 15mm Amalgamator

Analytical Curve
15 mm Amalgamator
3" Cell
Flow Rate 3
Variac 100%

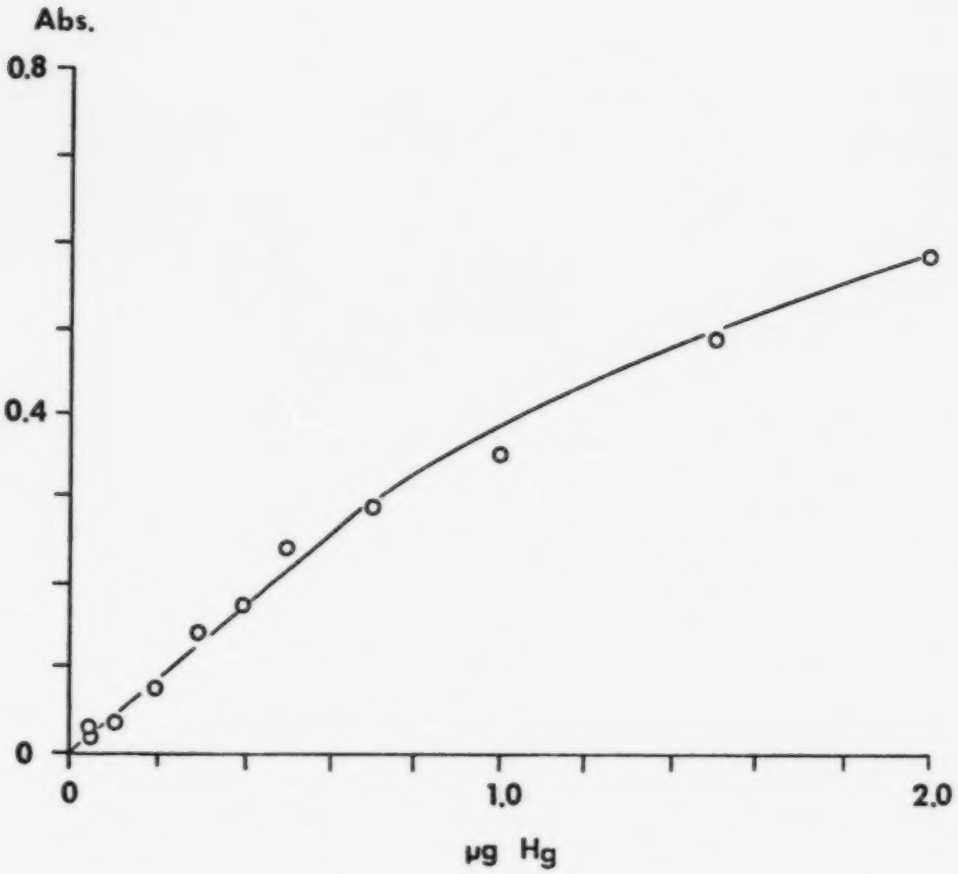


Figure 15. Analytical Curve obtained with 3" Cell and 15mm Amalgamator

Analytical Curve

25 mm Amalgamator

3" Cell

Flow Rate 1.5

Variac 45 %

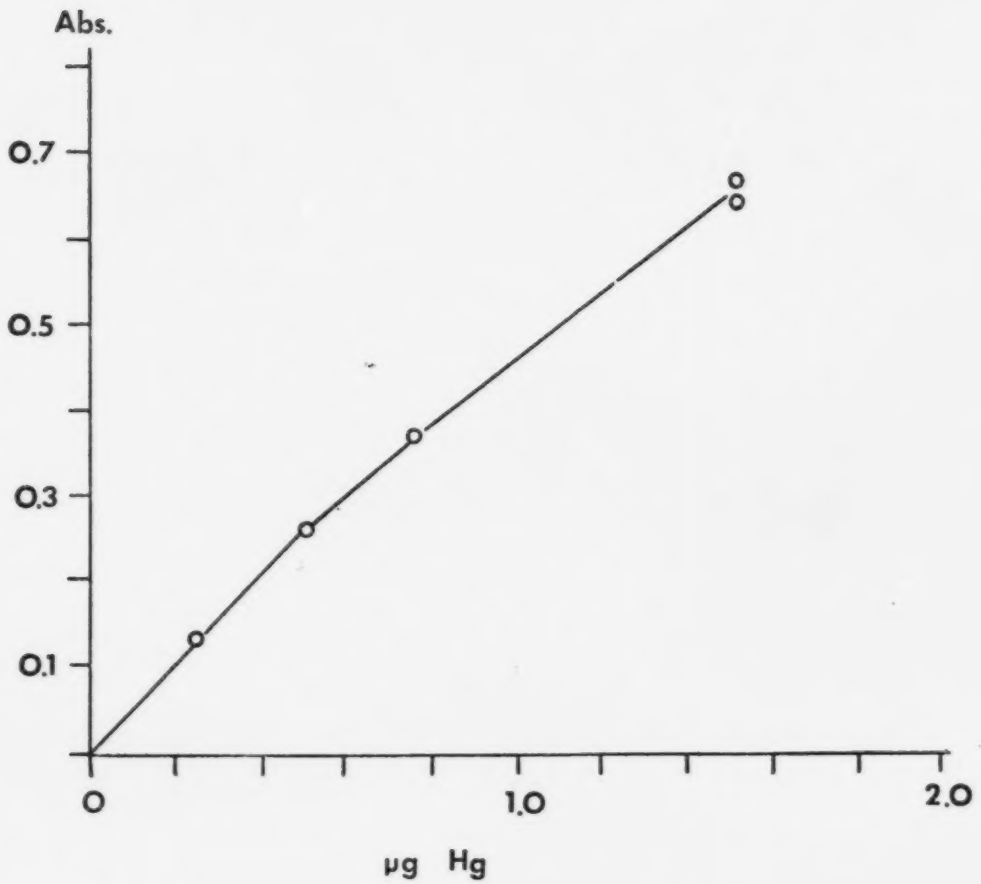


Figure 16. Analytical Curve obtained with 3" Cell and 25mm Amalgamator

STACK GAS SAMPLING

As discussed in the previous section, the amalgamators were designed to be inserted into a standard EPA isokinetic sampling train in place of the impingers. The interchangeable impingers and amalgamators permit using any combination of amalgamation and wet absorption techniques to verify collection efficiency of the various components. The isokinetic train is utilized to obtain a particulate sample simultaneously with the gas sample. Detectable levels in the particulate sample yield information on the condensation of the volatile mercury.

1- Preparation of the Amalgamators

When handling the gold wire and chips used in the amalgamators, care should be taken to keep the hands clean and free of oil or grease (such as stopcock grease picked up from handling the impingers). If grease is accidentally transferred to the gold it will be slowly released as the gold is fired, giving a false reading and a very irregular peak. The gold wire plug and chips to be used in the amalgamators should be cleaned before use. The best way of cleaning is to place the gold into small crucibles and fire it at about 750°C for three plus hours (or overnight). The cleaned gold may be stored for an indefinite period of time before use in small sealed (mercury free) vials.

To prepare the gold wire plug, 2 grams of gold wire are worked into a ball with the fingers. The wire is then rolled until it is slightly larger than the inside diameter of the amalgamation tube. The plug is then flattened into

a wafer and forced into the tube against the supporting fingers. A length of ¼" dowel rod and a stiff (about #10) wire are handy to help wedge the wad in place and flatten out any stray ends of wire. The gold plug should fit tightly enough in the tube to eliminate the bypass of any gold chips. After a wad has been used a few times, it may become loose in the tube. This may be corrected by removing it from the tube and spreading it slightly with the fingers and then repacking it with the dowel. After this has been done a few times the wad will become quite dense and tend to crumble. When this happens the wad may be pulled apart until it is separated into its original strands of wire. Enough new wire is added to make up 2 grams, and the plug is re-formed. In this way the plugs can be used almost indefinetely with only occasional addition of gold wire.

The gold chips may be prepared by cutting up a sheet of the metal, 0.007" thick, with a scissors or cutting board. The chips of gold should be about 1/8 to 1/16 inch square. Ten grams of gold chips are weighed and poured into the amalgamator on top of the plug, using a plastic funnel. The amalgamator is held vertically and gently tapped with the dowel to slightly compress the chips. When the amalgamator is packed, it is placed in the induction furnace and fired in the air stream to verify that the gold is "clean" (no absorption peak is registered on the recorder). After firing, the amalgamator is sealed by placing rubber stoppers in the ends of the tube. The plugs are removed just before the amalgamator is placed in the sampling train.

2- Operation of the Sampling Train

The sampling train predominantly utilized in this study consisted of a

5 foot glass probe heated to 150°F. with a 0.250" diameter tip. Samples were not collected isokinetically in the study permitting the probe tip to be pointed downstream (particulates were not routinely analyzed). The cyclone and filter were maintained at 200°F. Five impinger bases were used in an ice bath. The first impinger was a Greenburg-Smith type containing 300 ml. of an approximately 1% $SnCl_2$ in 4% HCl solution. This solution was prepared by adding 25 ml. of the stock $SnCl_2$ solution (used for reducing the standard solutions) and then diluting with distilled water. This reducing solution decreases any potential mercury absorption. The Greenburg-Smith impinger is used to decrease bubble size thus increasing gas contact with the solution. The solution is used to reduce the gas temperature below the dew point of sulfuric acid mist, removing SO_3, which is an apparent interference in the analytical procedure. The use of a $SnCl_2$ solution in the first impinger improved the original analyses, but the concentration and amount of the solution have not been optimized. The second impinger was empty and helped to remove some of the moisture from the gas stream. The third and fourth impingers each contained a gold amalgamator, one serving as a backup. The fifth impinger contained silica gel to remove the remaining water vapor before it entered the vacuum pump of the console unit.

After the sample is collected, the probe should be disconnected from the cyclone, the meter reading noted, and approximately one cubic foot of ambient air pulled through the unit (through the $SnCl_2$ solution) to assure complete volatilization of mercury from the solution. An aliquot of the $SnCl_2$ scrubbing solution should be preserved for analysis.

Although the particulate samples were not routinely analyzed in this study, the filter was replaced after each run and the probe rinsed periodically, depending on the particulate concentration of the stack. When samples are collected isokinetically the probe and cyclone should be rinsed with a 1:3 nitric acid-water solution, and the rinsings saved for analysis.

FIELD ANALYSES

After the analytical procedure was optimized, the following five areas were investigated with the stack gas samples:

(1) The efficiency of the gold procedure compared to an acidic permanganate solution absorption train. This was achieved by running Au-Au, Au-$KMnO_4$, and $KMnO_4$-Au trains. The permanganate solutions were prepared with nitric acid. ICl was not used because mercury volatilized from ICl solutions will not amalgamate onto gold requiring the elimination of the gold amalgamation step.

(2) A check for interferences, either other volatile compounds that also absorb 254 mμ radiation or compounds present in the system that absorb or adsorb mercury. The reaction of the gold with the gas stream must be considered to determine if it chemically absorbs any compounds from the gas stream or if volatile compounds condense on the gold.

(3) Analyses were performed at 5, 10, 15 and 30 minute sampling periods.

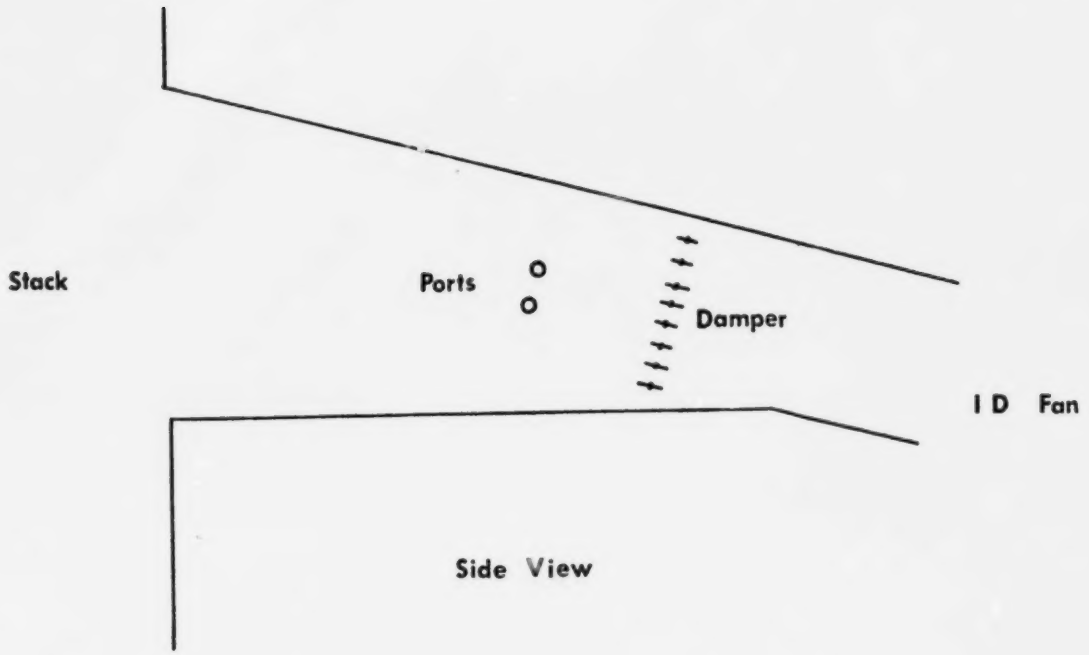
(4) Samples were collected at flows of 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 CFM. Samples were not collected isokinetically due to the location of the sampling ports and plant conditions at the first plant.

(5) A limited number of particulate samples were analyzed by (1) perchloric nitric digestion and flameless atomic absorption and (2) volatilization in the induction furnace accompanied by flameless atomic absorption.

Sampling sites at two different power plants were utilized for obtaining stack samples to investigate the above parameters under field conditions. A mobile laboratory permitting on site and instantaneous analyses of the samples was located at the first site for six weeks and at the second site for three days. The objective of the second site was to verify the results of the first site under different field conditions.

The first power plant utilized a mixed strip mine coal source predominantly from southeastern Ohio. Information obtained from the purchasing department showed the coal sources as: Ohio #5 seam 10%, Ohio #6 seam 40%, and Ohio #7 seam 40%. Samples were obtained in a 90,000 Kw single-train generator boiler. The unit is used as a peaking unit with a highly variable loading. A 50% change in loading was achievable within a few minutes. Maximum air utilization was 900,000 lbs./hr. Particulates in the stack gas were controlled by cyclone separators. Upon leaving the cyclones the gas passed through the ID fan, and then up the stack. The sampling site, illustrated in Figure 17, was located in a horizontal duct between the ID fan and the stack about 30 feet above the ground. A damper, used to control the draft, was located six feet upstream from the sampling ports and did result in a high degree of turbulence. The duct had a negative pressure ranging from 1 to 2 inches of water. At maximum plant operating conditions the gas temperature was approximately 325°F. at the sampling site. The mobile laboratory was located beneath the sampling site permitting the control console of the sampling train to be operated from within the laboratory.

The second site also utilized a mixed coal source but the mines were located



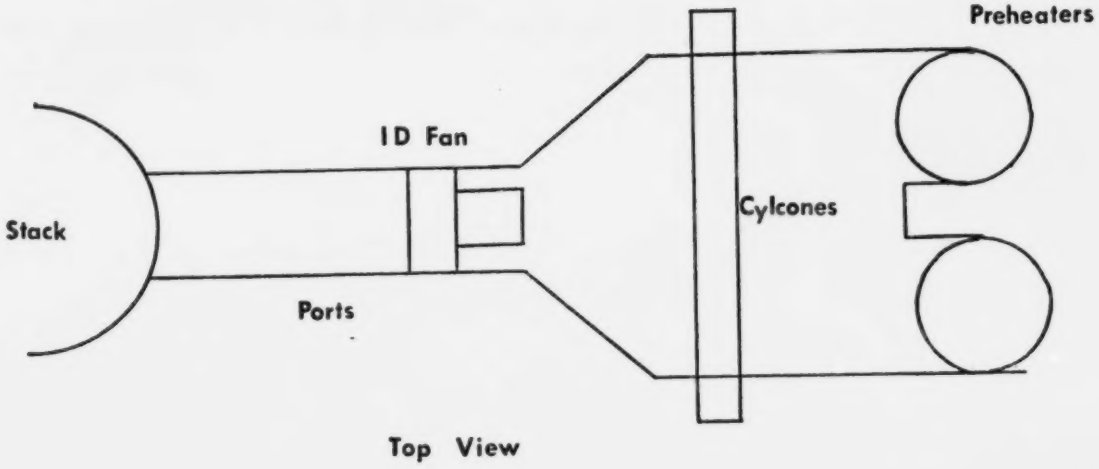


Figure 17. Physical Arrangement and Location of Ports at Site 1

in eastern Ohio. During the past few months the composition of this coal has averaged: Ohio #5 seam 10%, Ohio #6 seam 33%, Ohio #7 seam 3%, and Ohio-West Virginia #8 seam 54%. The unit that was sampled contained two boilers supplying one 86,000 Kw generator. The unit is normally operated at a constant loading resulting in a more advantageous sampling situation. Air usage was maintained between 300,000 and 350,000 lbs./hr. Particulates in the stack gas were controlled by a Western Precipitation electrostatic precipitator. Two banks of 4" sampling ports had been previously installed in rectangular ducts immediately before and after the electrostatic precipitator. The outlet ports were located between the precipitator and the ID fan. The perpendicular cross-section of the inlet duct is 5'0" x 22'8" with a velocity range of 12.2 to 51.6ft./sec., averaging 29.3 ft./sec. The outlet duct was 4'7 3/4" x 13'0" with a velocity range of 37.3 to 62.2 ft./sec., averaging 51.8 ft./sec. The static stack pressure was negative between 4 and 5 inches water with a slightly higher negative pressure on the outlet side. Under normal operating conditions the gas temperature at the ports was approximately 330°F. Samples were obtained at both the inlet and outlet ports.

STACK SAMPLING RESULTS

The observed mercury concentrations and the control parameters are presented in Tables 3 and 4 as a daily log of the runs. The results will be interpreted in relation to peak shapes, gold deterioration, interferences, absorption cell size, stack turbulence, length of runs, flow rate, observed concentrations and reproducibility.

1- Peak Shapes

As mentioned previously, a uniform release of mercury from the amalgam will result in a Gaussian or 'bell' shaped peak. For accurate determinations of the mercury concentration, the peaks resulting from standards should match the peaks resulting from the stack samples. In practice the standards took longer to be released from the amalgam and resulted in a lower, broader peak. This was a result of the stack gas samples being amalgamated from the top down (stack gas flow in the impingers of the train is down) and the standards being amalgamated up from the bottom. This situation is partially corrected by the additional step of reversing the direction of the air flow in the amalgamator while aerating the standard solutions. This results in amalgamating the volatile mercury by flow down through the amalgamator while both obtaining the sample and amalgamating the standard. Figure 18 illustrates an identical standard amalgamated from the top and from the bottom of the amalgamator and a typical stack gas sample. The potential error in the calculation of the stack sample is obvious. The firing of the induction furnace produces and induction field which interacts with

Table 3. Daily log of runs: mercury concentration and control parameters

SITE 1

DATE	TIME	SAMPLING TIME	SAMPLING RATE	VOLUME	IMPINGER ORDER	MERCURY				PREPEAKS		% RECOVERY
						AMAL. #1	AMAL.#2	TOTAL	CONCENTRATION	1	2	AMAL. #1
		minutes	CFM	liters		µg	µg	µg	µg/l	% abs.		
3/9/72	2:30	5	.762	107.8								
		5	.734	105.0								
		5	.664	94.0								
		5	.638	90.4								
		5	.767	108.5								
		5	.509	72.1								
		5	.579	82.0								
		5	.588	83.2								
3/10/72	2:30	5	.931	131.7								
		2.5	.349	24.7								
		2.5	.269	19.0								
	3:45	2.5	.297	21.0								
	4:05	2.5	.324	22.9								
		2.5	.307	21.7								
3/13/72	11:00	4.00	.372	41.7	A	1.3		1.3	.031	?		
	11:31	4.00	.397	44.5	A	0.5		0.5	.011	-		
	11:56	4.00	.344	38.4	A	0.74		0.74	.019	x		
	12:13	8.00	.484	108	A	0.21		0.21	.002	x		
	2:20	4.00	.452		A							
	4:15	5.00	.527		A							
3/14/72	11:34	5.00	.580	81.0	A	0.31		0.31	.0038	-		
	1:45	30.00	.565	475	A	0.3		0.3	.0006	-		
	2:41	30.00	.540	454	A	0.8		0.8	.0018	?		

SITE 1 (cont.)

DATE	TIME	SAMPLING TIME	SAMPLING RATE	VOLUME	IMPINGER ORDER	MERCURY				PREPEAKS		% RECOVERY
						AMAL. #1	AMAL. #2	TOTAL	CONCENTRATION	1	2	AMAL. #1
		minutes	CFM	liters		µg	µg	µg	µg/l	% abs.		
3/15/72	10:44	5.1	.067	9.6	AA							
	11:57	5.0	.065	9.2	AA							
	12:58	5.0	.064	9.1	AA							
	3:50	5.0	.073	10.3	EEA							
	4:33	5.0	.075	10.6	EEA							
	4:55	5.0	.076	10.7	EEA							
	5:15	5.0	.073	10.3	SEA							
	5:35	5.1	.071	10.2	SEA							
	5:57	5.5	.071	11.0	SEA							
3/16/72	4:15	5.0	.164	23.0	SEAA	0.50	0.10	0.60	.025	-	x	83
	5:36	5.0	.156	21.9	SEAA	0.27	0.16	0.43	.019	-	x	63
	6:33	5.0	.067	9.4	SEAA	0.19	0.36	0.55	.058	-	-	35
3/17/72	1:20	5.0	.078	10.9	SEAA	0.35	0.17	0.52	.048	x	x	67
	2:17	5.0	.081	11.3	SEAA	0.29	0.20	0.49	.044	5	-	59
	3:55	5.0	.080	11.2	SEAA	0.21	0.19	0.40	.036	-	-	52
	4:43	5.2	.080	11.6	SEAA	0.29	0.36	0.65	.056	-	-	45
3/20/72	11:08	5.0	.029	4.1	SEAA					59	83	
	11:46	5.0	.046	6.5	SEAA	0.146	0.059	0.205	.031	6	x	73
	12:18	5.0	.191	27.0	SEAA	0.48	0.006	0.49	.018	9	x	98
	12:58	5.0	.198	28.0	SEAA	0.29	0.054	0.34	.012	-	-	85
	1:35	5.0	.326	46.1	SEAA	1.1	0.074	1.17	.025	-	x	94
	2:26	5.0	.338	47.7	SEAA	0.94	0.093	1.03	.022	-	-	91
	3:03	5.0	.487	68.9	SEAA	1.35	0.06	1.41	.020	-	-	96
	3:45	5.0	.487	68.8	SEAA	1.57	0.096	1.67	.024	-	-	94
	4:18	5.0	.619	87.6	SEAA	1.52	0.25	1.77	.020	-	-	86
	4:52	5.0	.611	86.4	SEAA	1.49	0.29	1.78	.020	-	-	84
	5:32	5.0	.720	102.0	SEAA	1.58	0.54	2.12	.021	-	-	75
	6:03	5.0	.709	100.4	SEAA	0.67	0.70	1.37	.014	-	-	49
	6:35	5.0	.216	30.6	SEAA	0.18	0.12	0.30	.010	-	x	60

SITE 1 (cont.)

DATE	TIME	SAMPLING TIME	SAMPLING RATE	VOLUME	IMPINGER ORDER	MERCURY				PREPEAKS		% RECOVERY
						AMAL. #1	AMAL.#2	TOTAL	CONCENTRATION	1	2	AMAL. #1
		minutes	CFM	liters		µg	µg	µg	µg/l	% abs.		
3/21/72	11:00	5.0	.185	26.1	SEAA	0.44	0.017	0.46	.024	-	-	96
	11:44	5.0	.179	25.2	SEAA	0.14	0.025	0.17	.007	-	-	82
	12:27	5.0	.414	58.6	SEAA	0.55	0.038	0.59	.010	-	-	93
	1:08	5.0	.411	58.1	SEAA	0.61	0.086	0.70	.012	-	-	87
	1:43	5.0	.554	78.4	SEAA	1.13	0.12	1.25	.016	-	-	90
	2:30	5.0	.551	78.0	SEAA	1.26	0.14	1.40	.018	-	-	90
	3:11	5.0	.631	89.2	SEAA	1.35	0.12	1.47	.017	-	-	92
	3:50	5.0	.631	89.2	SEAA	1.28	0.13	1.41	.016	-	-	91
	4:48	5.0	.787	111.2	SEAA	0.22	0.22	0.44	.004	-	-	50
	5:29	5.0	.788	111.3	SEAA		0.27			79	x	-
3/22/72	10:21	5.0	.182	25.8	SEAA	0.46	0.22	0.68	.026	-	x	68
	11:16	5.0	.170	24.0	SEAA	0.24	0.70	0.94	.039	-	-	26
	12:02	5.0	.418	59.2	SEAA	0.81	0.10	0.91	.015	-	x	89
	2:44	5.0	.379	53.6	SEAA	1.40	0.10	1.50	.028	-	x	93
	3:22	5.0	.384	54.6	SEAA	1.04	0.18	1.22	.022	-	-	85
	3:49	5.0	.549	77.6	SEAA	1.23	0.35	1.58	.020	-	-	78
3/23/72	9:50	5.0	.213	30.2	SEAA	0.54	0.048	1.02	0.020	10	27	53
	10:18	5.0	.219	31.1	SEAA	0.30				-	34	
	10:42	5.0	.342	48.5	SEAA	1.20	0.04	1.24	0.026	-	8	97
	11:17	5.0	.343	48.6	SEAA	1.20	0.055	1.26	0.026	-	10.4	95
	11:57	5.0	.440	62.3	SEAA	1.29	0.09	1.38	0.022	-	1	94
	12:30	5.0	.442	62.5	SEAA	1.21	0.17	1.38	0.022	-	x	88
	1:00	5.0	.438	62.0	SEAA	1.3	0.20	1.50	0.024	-	5	87
	1:31	5.0	.508	71.8	SEAA	1.14	0.25	1.39	0.019	-	-	82
	2:00	5.0	.494	69.9	SEAA	1.1	0.25	1.35	0.019	?	-	82
	2:32	5.0	.608	86.0	SEAA	-						
	3:05	5.0	.587	83.9	SEAA	- gold deteriorating						
	4:00	10.0	.395	111.7	SEAA	2.6			0.023		70	
	5:12	10.0	.384	108.6	SEAA	- gold deteriorating						

SITE 1 (cont.)

DATE	TIME	SAMPLING TIME	SAMPLING RATE	VOLUME	IMPINGER ORDER	MERCURY				PREPEAKS		% RECOVERY
						AMAL. #1	AMAL. #2	TOTAL	CONCENTRATION	1	2	AMAL. #1
		minutes	CFM	liters		µg	µg	µg	µg/l	% abs.		
3/24/72	10:31	5.0	.488	69.1	SEAA	1.24	0.047	1.29	0.019	-	-	96
	11:14	5.1	.350	49.6	SEAA	1.04	0.025	1.06	0.021	-	x	98
	11:46	5.0	.583	82.6	SEAA	1.73	0.039	1.80	0.021	-	-	96
	12:32	5.0	.204	28.9	SEAA	0.30	0.088	0.39	0.013	-	-	77
	1:09	5.0	.703	99.6	SEAA	1.3	0.035	1.34	0.013	-	-	97
	1:48	5.0	.784	110.9	SEAA	2.2	0.054	2.25	0.020	-	-	98
	2:41	10.0	.202	57.2	SEAA	0.55				25	50	-
	3:22	10.0	.213	60.3	SEAA	0.56	0.13	0.69	0.011	-	-	81
	4:23	10.0	.350	99.1	SEAA	2.5	0.035	2.54	0.026	-	-	98
	5:00	10.0	.632	178.5	SEAA	>5.0	0.26			-	-	-
	5:54	10.0	.770	218.0	SEAA	>5.0	0.75			x	x	-
	6:40	10.0	.495	139.8	SEAA		0.17				-	-
3/25/72	10:30	10.0	.209	59.1	KEAA					x	x	-
	11:13	10.0	.335	94.7	KEAE						x	-
	12:10	10.0	.337	95.4	KEAE						x	-
	1:40	10.0	.338	94.5	KEAE	2.3		2.3	0.024			-
	3:20	10.0	.330	93.8	KEAE	1.96		1.96	0.021		80	-
	4:03	10.0	.318	90.0	KSEA	1.89	0.078	1.97	0.022		-	96
	5:10	7.0	.378	74.9	SEAK	1.9	0.22	2.12	0.028	16		90
	5:30	10.0	.243	68.6	KSEA	1.51	?	1.51	0.022		51	-
	6:20	7.0	.377	74.6	SEAK	1.1	0.21	1.3	0.018	x		85
3/27/72	12:15	15.1	.304	130.0	KSEA	2.59	0.69	3.28	0.025		-	79
	1:18	15.0	.291	123.4	SEAK	2.3	<0.5	<2.8	<0.023	-		-
	2:17	15.0	.443	188.0	SEAK	4.7	0.4	5.1	0.027	-		92
	3:05	15.0	.438	186.0	KSEA	3.93	0.59	4.52	0.024		4	87
	4:04	15.0	.575	244.0	KSEA	5.96	0.08	6.35	0.025		-	94
	5:34	15.0	.579	244.8	SEAK	4.68	0.65	5.33	0.022	-		88

SITE 1 (cont.)

DATE	TIME	SAMPLING TIME	SAMPLING RATE	VOLUME	IMPINGER ORDER	MERCURY				PREPEAKS		% RECOVERY
						AMAL. #1	AMAL.#2	TOTAL	CONCENTRATION	1	2	AMAL. #1
		minutes	CFM	liters		µg	µg	µg	µg/l	% abs.		
3/28/72	9:53	15.0	.681	289.5	SEAK	1.69	0.39	2.08	0.006	-		81
	10:49	15.0	.622	264.0	KSEA	4.43	0.16	4.59	0.025		-	97
	1:17	15.0	.478	203.0	KSEA	2.50	0.29	2.79	0.014		x	90
	2:00	15.0	.494	210.0	SEAK	1.85	0.9	2.95	0.013	-		68
	2:43	15.0	.320	136.0	SEAK	1.93	<0.3	1.93	0.014	x		90+
3/29/72	8:20	17.0	.395	189.9	SEAK	3.94	0.60	4.54	0.024	-	-	87
	9:02	17.0	.393	189.0	SEAK					-		-
	9:55	10.1	.395	113.0	SEAA					x	x	-
	11:00	10.0	.397	112.2	SEAA					x	x	-
	11:55	30.0	.386	328.0	SEAA							-
	2:16	5.0	.479	67.8	SEAA	1.19	0.167	1.36	0.020	10	x	88
	3:07	5.0	.469	66.4	SEAA	1.25	0.189	1.44	0.022	x	?	87
	3:52	5.0	.312	44.8	SEAA	0.58	0.04	0.62	0.014	5	14	93
3/30/72	11:10	5.0	.304	43.0	EEAA	0.063	0.046	0.109	0.003	15	17	58
	1:09	5.0	.297	42.0	HEAA	0.24	hidden		0.006	60	70	-
	2:34	5.0	.300	42.5	SEAA	0.46	hidden		0.011	20	62	-
	3:33	5.0	.297	42.0	AgEAA	0.12	0.21	0.33	0.008	64	x	36
	4:43	5.0	.510	72.2	SEAA	1.0	0.14	1.14	0.016	-	40	88
3/31/72	11:58	5.0	.340	48.1	HEAA	0.28				-	30.5	-
	12:42	5.0	.342	48.3	HEAA	0.29				-	16.5	-
	1:23	5.0	.340	48.1	HEAA					8	19.8	-
	2:15	5.0	.340	48.1	SEAA	0.79	0.073	0.863	0.018	-	15.2	92
	3:15	5.0	.328	46.5	SEAA	0.30	0.075	0.375	0.0081	-	5.6	81
	4:26	5.0	.329	46.5	SEAA	0.355	0.057	0.412	0.0088	-	4.5	86
	5:36	5.0	.328	46.5	HEAA	0.50	0.046	0.55	0.012	8.0	5.1	91
4/6/72	12:25	5.0	.473	40.8	SEAA	1.5	0.04	1.54	0.038	-	-	97

SITE 1 (cont.)

DATE	TIME	SAMPLING TIME	SAMPLING RATE	VOLUME	IMPINGER ORDER	MERCURY				PREPEAKS		% RECOVERY
						AMAL. #1	AMAL.#2	TOTAL	CONCENTRATION	1	2	AMAL. #1
		minutes	CFM	liters		µg	µg	µg	µg/l	%abs.		
4/7/72	10:50	5.0	.537	75.8	SEAA	0.60	0.29	0.89	0.012	-	x	68
	11:32	5.0	.568	80.4	SEAA	0.50	0.063	0.56	0.007	-	3	89
	12:03	5.0	.564	79.8	SEAA	0.44	0.62	1.06	0.013	x	x	41
	12:39	5.0	.559	79.1	SEAA	1.6	0.15	1.75	0.022	-	-	92
	1:10	5.0	.557	78.8	SEAA	1.44	0.32	1.76	0.022	-	15	82
	1:51	5.0	.546	77.3	SEAA	1.46	0.14	1.60	0.021	-	12	91
	2:28	5.0	.548	77.5	SEAA	0.55	0.23	0.78	0.010		x	71
	3:05	5.0	.538	76.1	SEAA	1.47	0.19	1.66	0.022			89
	3:40	5.0	.542	76.7	SEAA	1.57	0.43	2.00	0.026	-	-	79
	4:40	5.0	.409	58.0	SEAA	1.1	0.47	1.57	0.027	?	?	70
	5:10	5.0	.390	55.3	SEAA	0.95	0.67	1.62	0.027	5	?	59
	5:45	5.0	.367	52.2	SEAA	0.94	0.46	1.40	0.027	15	?	67
	6:30	5.0	.493	70.0	SEAA	1.13	0.19	1.32	0.019	-		86
	7:05	5.0	.488	69.0	SEAA	1.06	0.23	1.29	0.019			83
4/10/72	10:57	5.0	.382	54.1	SEAA	0.99	0.12	1.11	0.021	-	x	89
	11:39	5.0	.195	27.6	SEAA	0.55				x	-	-
	12:17	5.0	.531	75.1	SEAA	1.5	0.17	1.67	0.022	x	11	90
	12:48	5.0	.619	87.6	SEAA	1.43	0.41	1.85	0.021	-	x	78
	2:08	5.0	.767	108.3	SEAA	1.59	0.51	2.10	0.019	-	-	76
	2:42	5.0	.304	43.0	SEAA	0.48	0.32	0.80	0.019	-	25	60
	3:31	5.0	.304	43.0	SEAA	0.79	0.23	1.02	0.024	-	13	77
	4:00	5.0	.627	88.7	SEAA	0.89	0.62	1.51	0.017	-	-	59
	4:32	5.0	.770	109.0	SEAA	0.96	0.70	1.66	0.015	-	-	58
	5:10	5.0	.392	55.5	SEAA	0.29	0.66	0.95	0.016	-	x	31
	5:57	5.0	.399	56.5	SEAA	0.40	0.48	0.88	0.016	-	17	46
	6:27	5.0	.396	56.1	SEAA	0.45	0.58	1.03	0.018	-	17	44

SITE 1 (cont.)

DATE	TIME	SAMPLING TIME	SAMPLING RATE	VOLUME	IMPINGER ORDER	MERCURY				PREPEAKS		% RECOVERY
						AMAL. #1	AMAL.#2	TOTAL	CONCENTRATION	1	2	AMAL. #1
		minutes	CFM	liters		µg	µg	µg	µg/l	%abs.		
4/11/72	11:04	5.0	.402	56.9	SEAA	0.935	0.073	1.008	0.018	-	x	86
	11:45	5.0	.737	105.0	SEAA	1.20	0.046	1.25	0.012	-	-	96
	12:21	5.0	.734	104.0	SEAA					-	-	-
	1:40	5.0	.714	101.0	SEAA	0.52	0.16	0.68	0.0066	-	-	77
	3:26	5.0	.799	113.1	SEAA	0.86	0.11	0.97	0.0086	-	x	89
	4:21	5.0	.508	71.9	SEAA	1.1	0.09	1.19	0.017	-	6	93
	5:31	5.0	.259	36.6	SEAA	0.37	0.15	0.52	0.014	x	x	71
4/12/72	10:20	5.0	0.625	88.3	SEAA	1.84	0.18	2.02	0.023	-	x	91
	11:25	5.0	0.379	53.5	SEAA	0.78	0.02	0.80	0.015	x	x	97
	1:00	5.0	0.841	118.9	SEAA	1.56	0.27	1.83	0.015	-	-	85
	1:52	5.0	0.307	43.5	SEAA	0.27	0.42	0.69	0.016	-	x	39
	2:37	5.0	0.415	58.7	SEAA	0.85	0.0485	0.898	0.015	x	-	94
	3:21	10.0	0.423	119.7	SEAA	1.32	0.41	1.73	0.014	-	x	77
	4:10	15.0	0.383	162.4	SEAA	2.21	0.33	2.54	0.016	15	8	83
	5:10	5.0	0.427	60.3	SEAA	0.20	0.44	0.64	0.011	-	6	31
4/13/72	10:55	5.0	0.489	69.3	SEAA	1.33	0.33	1.66	0.024	-	-	80
	11:30	5.0	0.484	68.5	SEAA	0.42	0.35	0.77	0.011	-	-	55
	12:33	5.0	0.488	69.0	SEAA	0.84	0.08	0.92	0.013	-	-	91
	3:25	5.0	0.488	69.0	SEAA	0.46	0.18	0.64	0.0093	x	-	72
	4:17	5.0	0.500	70.6	SEAA	0.78	0.052	0.83	0.012	-	-	94
	5:05	15.0	0.470	199.0	SEAA	3.4	0.55	3.95	0.020	-	-	86

SITE 2

DATE	TIME	SAMPLING TIME	SAMPLING RATE	VOLUME	IMPINGER ORDER	MERCURY				PREPEAKS		%RECOVERY AMAL. #1
						AMAL. #1	AMAL.#2	TOTAL	CONCENTRATION	1	2	
		minutes	CFM	liters		µg	µg	µg	µg/l	%abs.		
4/19/72	10:35	5.0	0.500	77.6	SEAA	0.30	<0.01	0.30	0.0039	-	-	97+
	11:19	5.0	0.494	70.6	SEAA	0.21	<0.01	0.21	0.0030	-	-	95+
	11:55	10.0	0.511	144.0	SEAA	0.46	0.021	0.48	0.0033	-	-	96
	12:15	15.0	0.498	211.0	SEAA	2.06	0.031	2.09	0.0099	-	x	99
	2:11	15.0	0.510	216.0	SEAA	2.10	0.45	2.55	0.0120	x	-	83
	3:23	10.0	0.511	144.7	SEAA	0.65	0.50	1.15	0.0079	-	-	57
	8:30	5.0	0.509	72.1	SEAA	0.20	<0.01	0.20	0.0028	-	-	95+
	9:00	5.0	0.506	71.6	SEAA	0.45			0.0063	-	x	-
	9:33	5.0	0.519	73.4	SEAA	0.37	0.016	0.39	0.0052	x	10	95
4/20/72	9:47	10.0	0.492	139.1	SEAA	0.90	0.054	0.95	0.0068	-	20	95
	10:33	10.0	0.506	143.2	SEAA	0.89	0.05	0.94	0.0066	-	47	95
	11:17	10.0	0.322	85.0	SEAA	0.46	---	0.46	0.0054	10	40	-
	12:04	10.0	0.328	92.7	SEAA	0.29	---	0.29	0.0031	6	40	-
	12:51	10.0	0.723	204.5	SEAA	0.78	0.47	1.25	0.0061	-	-	62
	2:16	10.0	0.804	228.0	SEAA	1.06	0.05	1.11	0.0049	-	x	96
	2:59	5.0	0.734	104.0	SEAA	0.46	0.033	0.49	0.0047	-	4	94
	3:39	5.0	0.496	70.2	SEAA	0.345	0.012	0.357	0.0050	-	-	97
	4:33	5.0	0.394	55.9	SEAA	0.274	0.056	0.33	0.0059	-	3	82
	5:13	5.0	0.721	102.0	SEAA	0.43	0.02	0.45	0.0044	-	-	95

Impinger Order: A - gold
Ag- $AgNO_3$ scrubber
E - empty
H - water scrubber
K - $KMnO_4$ scrubber
S - $SnCl_2$ scrubber

Prepeaks: - - absent
x - present, but not measurable

Table 4. Daily log of runs: control parameters

DATE	TIME	DRY GAS TEMP.	AMALGAMATOR	GOLD		STACK CONDITIONS			INSTRUMENT PARAMETERS			AMBIENT TEMP.
				CONDITION	AMOUNT	STATIC PRESSURE	TEMP.	AIR FLOW	AIR FLOW Perkin-Elmer	CELL SIZE	FIRING TEMP.	
		°F	mm		grams	inches H_2O	°F	lbs./hr.	units	inches		°F
3/9/72	2:30	63				2.3	330					
		69				2.2	330					
		77				1.9	330					
		83				1.6	330					
		89				1.2	330					
		92				0.46	325					
		94				0.38	320					
		95				0.11	325					
3/10/72	2:30	66				1.7	335		3		75%	
		63				1.6	330					
		64				1.5	325					
	3:45	66				1.6	325					
	4:05	67				1.6	320					
		68				1.6	325					
3/13/72	11:00	70	25		10	1.5	320	920,000	4	3"	75%	71
	11:31	75	15			1.5	310	760,000			85%	
	11:56	77	25			1.7	305	700,000			65%	
	12:13	83	15			1.6	305	820,000			85%	
	2:20	79	15			1.7	310	620,000			80%	
	4:15	74				1.5	305	770,000				
3/14/72	11:34	66	15			1.5	340	900,000	1.5	3"	82%	35
	1:45	92	15			1.6	340	700,000				
	2:41	97	15			1.4	340	760,000				
3/15/72	10:44	63	15	F	15, 20	2.1	330	840,000	1.5	3"	82%	35
	11:57	64		-	15, 20	2.2	320	800,000				
	12:58	67		-	15, 20	2.0	320	810,000				
	3:50	69		F	15	1.9	320	740,000				
	4:33	70		-	15	1.4	320	610,000				

DATE	TIME	DRY GAS TEMP.	AMALGAMATOR	GOLD		STACK CONDITIONS			INSTRUMENT PARAMETERS			AMBIENT TEMP.
				CONDITION	AMOUNT	STATIC PRESSURE	TEMP.	AIR FLOW	AIR FLOW Perkin-Elmer units	CELL SIZE inches	FIRING TEMP.	
		°F	mm		grams	inches H_2O	°F	lbs./hr.				°F
3/15/72	4:55	71	15	-	15	1.5	320	555,000	1.5	3"	82%	35
	5:15	71		-	15	1.5	320	555,000				
	5:35	71		-	15	1.4	320	555,000				
	5:57	71		-	15	1.9	320	680,000				
3/16/72	4:15	75	15	F		1.5	315	760,000	1.5	3"	82%	50
	5:36	71				1.3	320	540,000				
	6:33	70				1.3	315	540,000				
3/17/72	1:20	-	15	F		2.0	325	740,000	1.5	3"	82%	40
	2:17	78				1.6	335	540,000				
	3:55	77				1.8	330	650,000				
	4:43	78				1.6	330	550,000				
3/20/72	11:08	65	15	F	10	1.5	325	610,000	1.5	3"	82%	-
	11:46	66		-		1.9	325	870,000				
	12:18	68		-		1.9	325	610,000				
	12:58	70		-		1.5	310	610,000				
	1:35	74		-		1.5	310	620,000				
	2:26	75		-		1.2	280	440,000				
	3:03	79		-		1.1	275	240,000				
	3:45	81		-		1.1	270	170,000				
	4:18	84		-		1.0	260	170,000				
	4:52	85		-		1.0	260	300,000				
	5:32	85		-		1.0	265	300,000				
	6:03	85		-		1.0	270	280,000				
	6:35	79		-		1.2	280	450,000				
3/21/72	11:00	68	25	F	12	1.2	270	420,000	1.5	3"	45%	-
	11:44	73				0.9	250	280,000				
	12:27	77				0.9	250	280,000				
	1:08	79				1.2	275	640,000				

DATE	TIME	DRY GAS TEMP.	AMALGAMATOR	GOLD		STACK CONDITIONS			INSTRUMENT PARAMETERS			AMBIENT TEMP.
				CONDITION	AMOUNT	STATIC PRESSURE	TEMP.	AIR FLOW	AIR FLOW Perkin-Elmer units	CELL SIZE inches	FIRING TEMP.	
		°F	mm		grams	inches H_2O	°F	lbs./hr.				°F
3/21/72	1:43	83	25	F	12	1.3	285	630,000	1.5	3"	45%	
	2:30	84				1.2	280	420,000				
	3:11	86				1.0	270	390,000				
	3:50	85				1.1	270	380,000				
	4:48	84				1.8	305	700,000				
	5:29	81				1.4	305	580,000				
3/22/72	10:21	60	25	F	24, 12	1.5	315	670,000	1.5	3"	45%	-
	11:16	63		F	12, 24	1.4	325	580,000			45%	
	12:02	65		HNO_3	12	1.3	320	550,000			45%	
	2:44	65		HNO_3		1.4	325	590,000			50%	
	3:22	65		HNO_3		1.3	325	560,000			50%	
	3:49	67		HNO_3		1.3	325	560,000			50%	
3/23/72	9:50	56	15	F	10	1.8	340	680,000	3	3"	80%	30
	10:18	58		F		2.0	350	830,000				
	10:42	60		F		2.0	350	900,000				
	11:17	62		HNO_3		2.0	355	860,000				
	11:57	62		↓		2.0	355	760,000				
	12:30	63				1.9	355	840,000				
	1:00	64				1.9	350	800,000				
	1:31	64				2.0	340	900,000				
	2:00	65				2.0	355	790,000				
	2:32	65				1.9	350	840,000				
	3:05	66				2.1	350	800,000				
	4:00	66				2.0	365	920,000				
	5:12	64				1.8	360	670,000				
3/24/72	11:31	56	15	F	10	2.1	355	760,000	3	3"	85%	-
	11:14	58		F		2.1	345	810,000				
	11:46	63		F			345	810,000				

DATE	TIME	DRY GAS TEMP.	AMALGAMATOR	GOLD		STACK CONDITIONS			INSTRUMENT PARAMETERS			AMBIENT TEMP.
				CONDITION	AMOUNT	STATIC PRESSURE	TEMP.	AIR FLOW	AIR FLOW Perkin-Elmer units	CELL SIZE	FIRING TEMP.	
		°F	mm		grams	inches H_2O	°F	lbs./hr.		inches		°F
3/24/72	12:32	66	15	F	10	2.1	340	870,000	3	3"	85%	
	1:09	75		HNO_3		1.9	345	820,000				
	1:48	76		↓		2.0	340	840,000				
	2:41	76				2.1	345	820,000				
	3:22	-				1.4	330	530,000				
	4:23	71				2.0	340	910,000				
	5:00	80				1.5	330	520,000				
	5:54	83				1.5	330	530,000				
	6:40	76				1.7	330	720,000				
3/25/72	10:30	56	15	F	10	2.1	360	980,000	3	3"	85	33
	11:13	67		F		2.1	360	980,000				
	12:10	71		HNO_3		2.0	355	980,000				
	1:40	75		↓		2.1	360	820,000				
	3:02	74				2.1	345	730,000				
	4:03	75				1.8	330	700,000				
	5:10	75				2.1	340	900,000				
	5:30	76				2.1	345	820,000				
	6:20	77				-	355	960,000				
3/27/72	12:15	64	15	F	10	1.9	350	940,000	3	½"	90%	47
	1:18	71		F		1.9	345	970,000				
	2:17	76		F		1.9	340	970,000				
	3:05	76		F		1.8	350	970,000				
	4:04	80		HNO_3		1.8	350	970,000				
	5:34	79		HNO_3		1.8	355	970,000				
3/28/72	9:53	70	15	F	10	2.1	360	980,000	3	½"	90%	42
	10:49	74		F		2.1	360	980,000				
	1:17	82		F		1.9	340	900,000				
	2:00	81		HNO_3		2.0	345	980,000				
	2:40	80		↓		2.0	350	980,000				

DATE	TIME	DRY GAS TEMP.	AMALGAMATOR	GOLD		STACK CONDITIONS			INSTRUMENT PARAMETERS			AMBIENT TEMP.
				CONDITION	AMOUNT	STATIC PRESSURE	TEMP.	AIR FLOW	AIR FLOW Perkin-Elmer units	CELL SIZE	FIRING TEMP.	
		°F	mm		grams	inches H_2O	°F	lbs./hr.		inches		°F
3/29/72	8:20	73	15	F	10	1.9	340	870,000	2	½"		43
	9:02	82		F		1.9	340	940,000		½"		
	9:55	79		F		2.0	350	920,000		½"		
	11:00	75		HNO_3		1.8	340	850,000		½"		
	11:55	92		HNO_3		1.9	340	820,000		½"		
	2:16	82		HNO_3		1.8	330	780,000		3"		
	3:07	77		HNO_3		1.9	320	780,000		3"		
	3:52	75		HNO_3		1.8	335	550,000		3"		
3/30/72	11:10	59	15	F	10	1.5	320	600,000	2	3"	100%	47
	1:09	66		F		1.4	315	620,000				
	2:34	72		HNO_3		1.2	310	540,000				
	3:33	74		HNO_3		1.3	310	560,000				
	4:43	76		HNO_3		1.3	300	440,000				
3/31/72	11:58	65	15	F	10	1.2	270	240,000		3"		52
	12:42	64		F		1.2	265	240,000				
	1:23	82		F		1.1	270	240,000				
	2:15	86		HNO_3		1.1	270	240,000				
	3:15	87		HNO_3		1.2	270	240,000				
	4:26	68		HNO_3		1.1	265	240,000				
	5:36	66		HNO_3		1.2	270	240,000				
4/6/72	12:25	60	15	F	10	1.1	280	490,000	double amalgamation			
4/7/72	10:50	53	15	F	10	-	320	600,000	3	3"	90%	26
	11:32	56		F		1.9	320	600,000				
	12:03	-		F		1.5	330	600,000				
	12:39	64		HNO_3		-	340	760,000				
	1:10	63		↓		1.6	340	700,000				
	1:51	63		↓		1.5	320	680,000				

DATE	TIME	DRY GAS TEMP.	AMALGAMATOR	GOLD		STACK CONDITIONS			INSTRUMENT PARAMETERS			AMBIENT TEMP.
				CONDITION	AMOUNT	STATIC PRESSURE	TEMP.	AIR FLOW	AIR FLOW Perkin-Elmer	CELL SIZE	FIRING TEMP.	
		°F	mm		grams	inches H_2O	°F	lbs./hr.	units	inches		°F
4/7/72	2:28	62	15	HNO_3	10	1.5	325	680,000	3	3"	90%	26
	3:05	63		↓		1.8	340	770,000				
	3:40	64				1.7	340	770,000				
	4:40	61				1.5	335	650,000				
	5:10	62				1.4	325	640,000				
	5:45	62				1.6	335	650,000				
	6:30	62				1.8	340	710,000				
	7:05	62		↓		-	360	980,000				
4/10/72	10:57	64	15, 25	F	10	1.7	310	705,000	3	3"	100%-55%	58
	11:39	68		F		1.8	310	705,000				
	12:17	73		F		1.8	310	705,000				
	12:48	77		HNO_3		1.8	310	710,000				
	2:08	81		↓		1.7	315	700,000				
	2:42	79				1.8	320	850,000				
	3:31	75				1.9	320	850,000				
	4:00	78				1.8	325	850,000				
	4:32	80				1.8	330	850,000				
	5:10	75				1.9	330	780,000				
	5:57	72				1.9	335	780,000				
	6:27	72		↓		1.9	330	740,000				
4/11/72	11:04	72	15	F	10	1.9	320	720,000	3	3"	100%	65
	11:45	77		F		1.7	315	700,000				
	12:21	79		F		1.8	305	650,000				
	1:40	78		HNO_3		1.9	305	680,000				
	3:26	77		↓		1.6	305	520,000				
	4:21	76				1.9	320	710,000				
	5:13	75		↓		1.8	320	700,000				

DATE	TIME	DRY GAS TEMP.	AMALGAMATOR	GOLD		STACK CONDITIONS			INSTRUMENT PARAMETERS			AMBIENT TEMP.
				CONDITION	AMOUNT	STATIC PRESSURE	TEMP.	AIR FLOW	AIR FLOW Perkin-Elmer	CELL SIZE	FIRING TEMP.	
		°F	mm		grams	inches H_2O	°F	lbs./hr.	units	inches		°F
4/12/72	10:20	64	15	F	10	2.0	325	850,000	3	3"	100%	64-73
	11:25	72		F		1.8	325	880,000				
	1:00	80		F		1.9	315	830,000				
	1:52	79		HNO_3		1.8	320	680,000				
	2:37	79		↓		1.6	305	690,000				
	3:21	83				1.9	310	690,000				
	4:10	90				1.9	310	700,000				
	5:10	84				1.3	300	520,000				
4/13/72	10:55	74	15	F	10	1.7	330	960,000	3	3"	100%	72
	11:30	79		F	10	-	325	960,000				
	12:33	81		F	10	1.9	320	820,000				
	3:25	84		F	10	1.9	305	780,000				
	4:17	86		HNO_3	17.5, 10	1.9	310	800,000				
	5:05	92		HNO_3	17.5, 10	1.9	320	800,000				
4/19/72	10:35	83	15	F	15	4.9	320	340,000	3	3"	80%	
	11:19	85		F		4.8	320	350,000				
	11:55	88		F		4.9	320	↓				
	12:51	94		HNO_3		5.0	320					
	2:11	94		HNO_3		4.9	320					
	3:23	91		HNO_3		4.8	320					
	8:30	86		[illegible]		4.7	310					
	9:00	88		F		4.9	310					
	9:33	89		F		4.9	315	↓				
4/20/72	9:47	75	15	F	15	4.2	340	300,000	3	3"	80%	
	10:33	84		F		4.2	330	↓				
	11:17	86		F		4.3	330					
	12:04	84		F		4.2	330					
	12:51	88		F		4.1	330					
	2:16	86		F		4.3	330	↓				

DATE	TIME	DRY GAS TEMP.	AMALGAMATOR	GOLD		STACK CONDITIONS			INSTRUMENT PARAMETERS			AMBIENT TEMP.
				CONDITION	AMOUNT	STATIC PRESSURE	TEMP.	AIR FLOW	AIR FLOW Perkin-Elmer	CELL SIZE	FIRING TEMP.	
		°F	mm		grams	inches H_2O	°F	lbs./hr.	units	inches		°F
4/20/72	2:59	85	15	F	15	4.1	330	300,000	3	3"	80%	
	3:39	83		F		4.3	330	↓				
	4:33	81		F		3.9	340					
	5:13	83		F		3.8	330					

Gold Condition: - - not cleaned
F - fired at 750°C
HNO_3 - rinsed in boiling nitric acid for 5 minutes

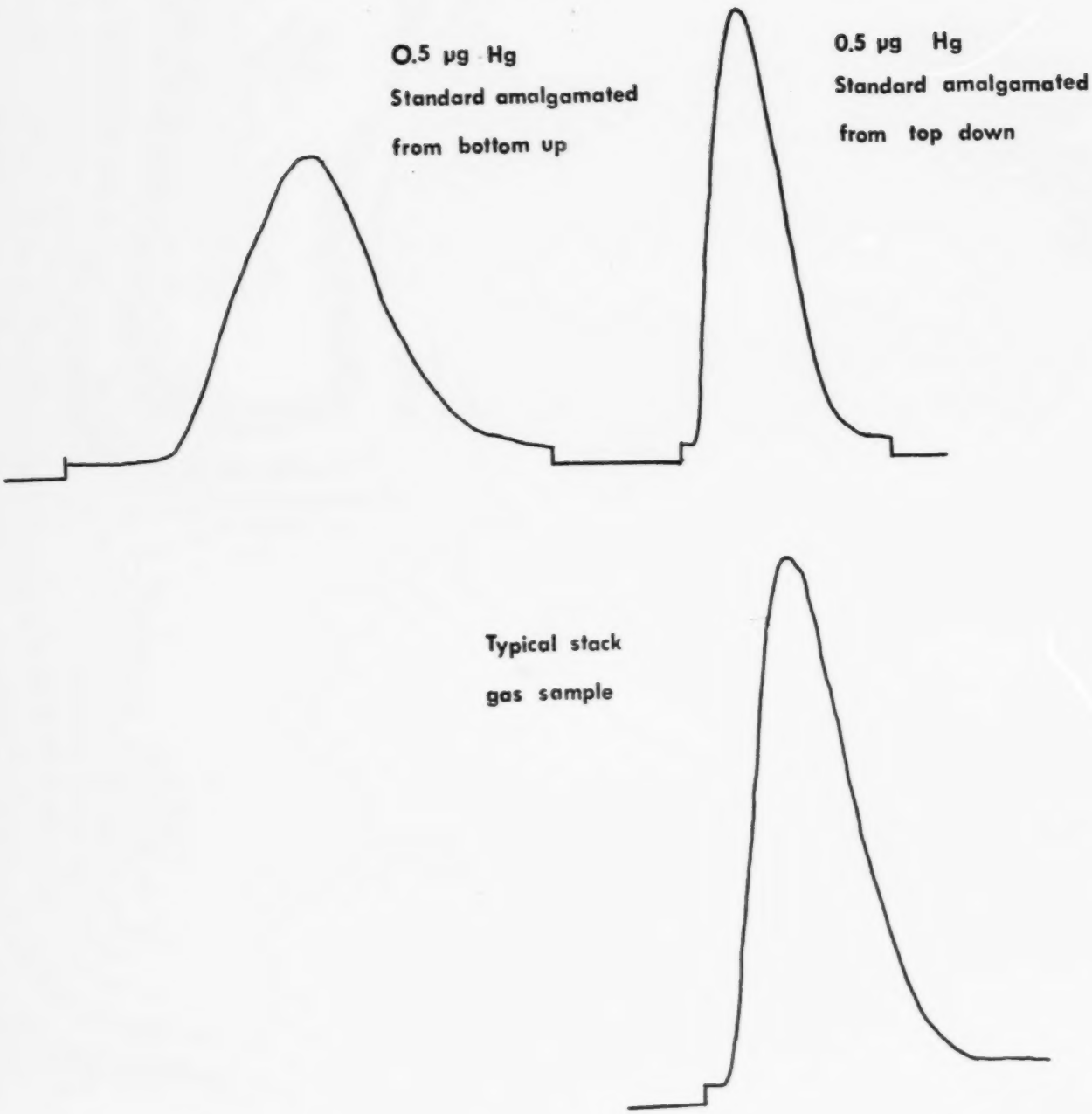


Figure 18. Illustration of Differences observed in Peak Shape due to amalgamating the Standard from the botton up or the top down

the electronics of the recorder resulting in the initial jump of 1 to 3% of the recorder paper observed in the figure. This permits an accurate way to measure the time involved from initial firing until the curve peaks. The figure illustrates the increased time required for the bottom amalgamated standard to peak. The difference in the direction of amalgamation does verify that we are not saturating the gold with mercury.

These initial results have shown that the manner in which the mercury is amalgamated is critical. Considering that the sample is amalgamated at a high velocity and a relatively low concentration and the standard is amalgamated at a low velocity and a high concentration it is obvious that the standards and samples cannot be perfectly matched. The standards and samples can be matched exactly if a double amalgamation procedure is adopted.

Periodically doublets and prepeaks occur. It is presently the opinion of the investigators that a sharp prepeak on either the first or second amalgamator is the result of water. Water is known to absorb 254 mμ radiation. The water is present from two sources; (1) condensation, and (2) chemical breakdown during firing in the induction furnace. Water was observed as a severe interference during cold weather. During these climatic conditions water would condense and run down the sides of the impinger-amalgamator during sampling and during the initial removal of the amalgamator from the train. This water was trapped by the gold foil and wire. This condition would also be a factor of the percent moisture in the stack. When the amalgamator was fired the water volatilized before the mercury and formed the prepeak. This is eliminated by drying the amalgamator before analyses. The second source

appears to be from the firing of H_2SO_4 condensed on the gold. At times these prepeaks occur repeatedly, but generally they appear to occur randomly, usually from only one of the two amalgamators. If we are near the dew point of sulfuric acid mist this would account for this phenomenon occurring on only one of the amalgamators. The prepeaks are distinguished from the true mercury peaks by their sharpness and quickness in being volatilized during firing. Figure 19 contains a sample peak illustrating the prepeak, and a peak obtained from a standard solution. The theoretical water peak may be distinguished from the mercury by measuring the time evolved from the start of firing. This is illustrated in the figure permitting easier interpretation of the results. A slightly lower firing temperature tends to further separate the two peaks. A magnesium perchlorate drying tube was inserted between the amalgamator and the absorption cell which did eliminate the prepeak while in use. After several good runs it also absorbed the mercury.

Periodically doublets will occur near the top of the mercury peak. Both peak tops are similarly shaped and do correspond to the standard in both shape and time evolved after firing. The doublets are similar to those observed with standards in the ½" cell. These are a function of the amalgamation reaction and the accompanying release during firing of the amalgam. The doublet would be eliminated by either using a larger volume cell or by double amalgamations.

2- Interferences

Interferences may be classed as (1) also absorbing 254 m μ radiation, or

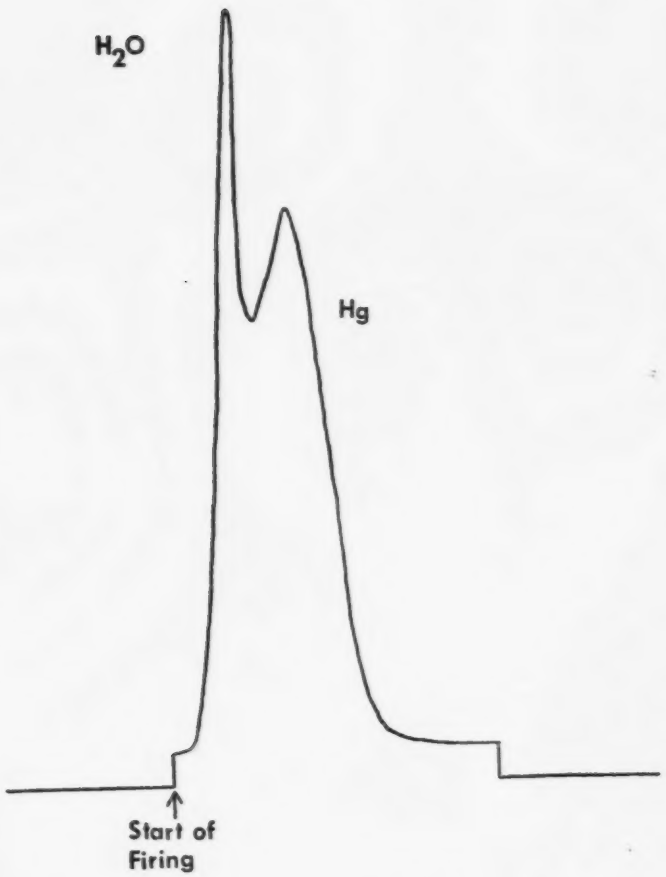


Figure 19. Illustration of a high Prepeak due to Water Absorption resulting from the chemical breakdown of Sulfuric Acid during firing.

(2) prohibiting the mercury from reaching the absorption cell by either a chemical reaction or physical adsorption. Water, resulting from condensation on and above the gold in the amalgamator, does produce a prepeak which may be distinguished from mercury or eliminated by drying. Condensed sulfuric acid mist evolves water vapor during firing and also appears to absorb a portion of the volatile mercury. When a sample containing this interference is fired the prepeak is observed and a white precipitate forms on the amalgamator wall above the induction coil. The white precipitate is water soluble and the wash solution is very acidic and contains mercury when analyzed by the same procedure as the standard. It is our theory that the white material is recondensed sulfuric acid mist containing some mercuric sulfate. Sulfuric acid has been added dropwise to the gold and then fired producing identical results. These washings from the amalgamator precipitated with barium produced a sulfate x-ray pattern. Verification of this interference has been difficult due to its irrational periods of occurrence. The $SnCl_2$ scrubber solution in the first impinger was added to the sampling train to eliminate this interference. It greatly decreased the observable amounts of the white precipitate but did not completely eliminate it or the prepeak. Insufficient time was available to optimize the scrubber solution or to try several other procedures including rinsing the gold with water and redrying it between sampling and firing in the induction furnace. The United States Geological Survey developed a method for directly amalgamating mercury out of water solutions strongly suggesting that the amalgam is stable in water.[10]

3- Gold Deterioration

Gold deterioration can result from (1) chemical reactions with constituents of the stack gas stream and (2) physical adsorption or condensation of volatiles in the gas stream which are either chemically broken down or not completely revolatilized during firing. Gold is a very stable element and forms very few compounds. It does form the chloride. AuCl decomposes to $AuCl_3$ at 170°C. $AuCl_3$ melts at 254°C and sublimes at 265°C. To verify the existence of chlorine and/or chloride in the stack gases the first impinger was filled with a silver nitrate solution. The solution turned white immediately upon the start of sampling. Joensuu[9] has mentioned chloride as an interference in the double gold procedure for mercury in coal, and he eliminates it by collection on heated silver foil as the chloride. (The silver chloride is stable to much higher temperatures than the gold chloride.) The results obtained in this study have not shown any reaction specifically designating chloride as adversely affecting the gold. The $SnCl_2$ solution in the first impinger would theoretically reduce any chlorine to the water soluble chloride. A large amount of chlorine could deplete the reducing capability of the stannous chloride accounting for the small mercury residue observed in the scrubber solution after sampling.

The gold does deteriorate with increased usage in the stack. The peaks of standards run on gold used extensively in the stack show a lowering and broadening of the peak. Additional firing of the gold after the mercury peak has returned to base level with old gold results in a second low broad peak. Initially the gold was boiled in concentrated nitric acid after each usage

in the sampling train. This did not rejuvenate the gold. Firing in an oven at 750°C for three plus hours did rejuvenate the gold. The reaction accounting for this is unknown. Condensation of volatile organics, etc., on the gold is a possibility. Gold deterioration does not increase at a constant rate but appears to be a function of the coal used and the firing efficiency of the boiler. Some days the gold will retain its sensitivity for the complete day, other days it will be good for only two to three runs. From the unpredictable results that were observed it is suggested that the gold should be fired in an oven after each usage in the stack. Based on the studies at these two power plants this precaution will eliminate any problems from gold deterioration.

4- Absorption Cell

The maximum concentration obtainable in the linear portion of the analytical curve with the 3" and 6½" absorption cell is approximately 1 µg per sample. This corresponds to a 5 to 10 minute sampling period at isokinetic rates. The ½" cell permits analyzing up to 7 - 10 µg, which would be acceptable for extended isokinetic sampling. This cell, which approximates measuring concentrations instead of total mercury, accentuates any doublets or other idiosyncrasies in the peak shape. For this cell to be used as a peak height cell the mercury must be distributed identically and evenly with each sample and standard. This cannot be achieved with the present procedure. Modifications permitting this desensitized cell to be used would include (1) double amalgamation and (2) a mixing chamber between the induction furnace and the absorption cell. Alternate methods, decreasing the

sensitivity, include a high volume peak height cell with a short optical path and a cycling system. Complete mixing is critical in the high volume cell, and some form of baffles to assure mixing would probably be required.

As has been shown, the standard method of desensitizing an analytical optical system by shortening the path length is not directly applicable in these circumstances. Based on these results the Laboratory Data Control mercury unit would require some extensive modifications and studies before it could be used. This problem and some of the other problems encountered may be solved by using a cycling system where the measured mercury concentration would be a function of the available space in the cycling system. In practice, the sample would be fired identically to the present procedure. The mercury would then by cycled through the cell with a small pump until equilibrium was achieved. The sensitivity of the system would be directly related to the volume that the sample is cycled through. This would permit using any of the described cells and also the Laboratory Data Control unit. This would eliminate the need for double amalgamation and would greatly desensitize the system permitting extended sampling periods.

5- Stack Turbulence

Stack turbulence, very prevalent at the first plant, may affect the efficiency of removal of mercury on the first amalgamator. Increased turbulence may cause a proportional increase in bypass of the first amalgamator, resulting in a greater mercury recovery on the second or backup amalgamator. No attempt was made to obtain a quantitative measure of the turbulence.

The turbulence was qualitatively interpreted from fluctuations observed in the static stack pressure during sampling and from the air flow recordings obtained from the plant. Increases or decreases in loading occurred frequently at the first plant and resulted in changes in the speed of the ID fan and the damper setting. Any problems resulting from turbulence may be corrected by increasing the amount of gold.

6- Sampling Period

Samples were obtained and analyzed at 5, 10, 15, and 30 minute sampling periods. The analytical interpretation of the data became progressively more difficult the longer the sampling period due to (1) working in the nonlinear section of the analytical curve, and (2) the increased likelihood of turbulence and interferences. Gold deterioration was not observed with the longer runs, but this may have been masked by other problems. Figure 20 illustrates the effect of increased sampling periods. Under optimum conditions the values are very consistent. The results must be compared on a daily basis due to bin loading occurring every one or two days resulting in a different grade of coal at both of the plants investigated. Analyses of coal samples from these seams obtained through the United States Bureau of Mines 'round robin' have shown a range of 0.1 to 0.44 ppm mercury, a four fold difference.

7- Flow Rates

Samples were collected non-isokinetically at 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 CFM. Figure 21 illustrates the effect of flow rate as a function of the observed concentration (concentrations are not corrected for

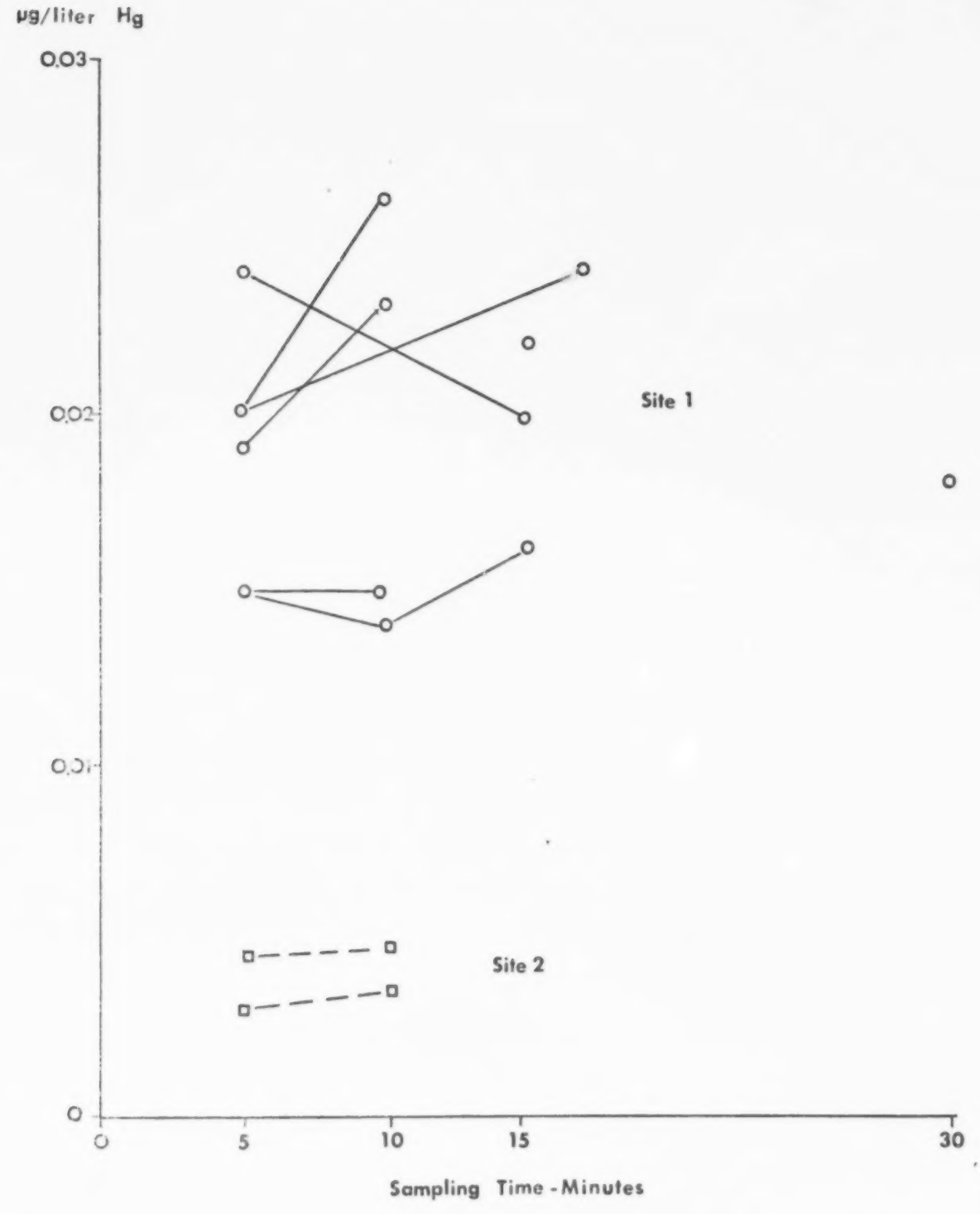


Figure 20. The Observed Mercury Concentration as a Function of Sampling Time

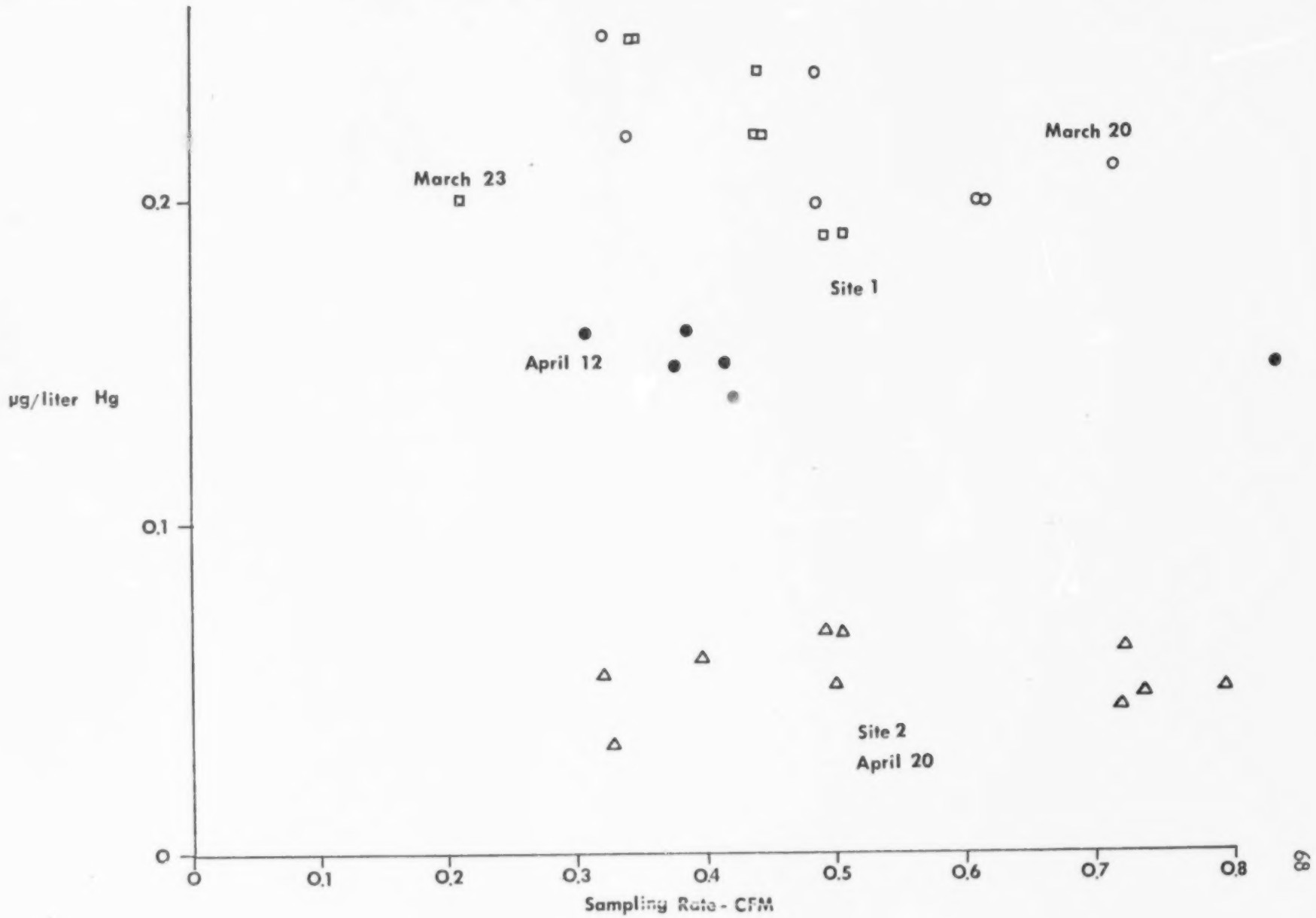


Figure 21. The Observed Mercury Concentration as a Function of Sampling Rate.

standard atmospheric conditions). Although there is a general fluctuation of the concentrations, there appears to be no significant difference in the recovery ratios at the various sampling rates. This should be reverified at a plant operating at a constant loading and with a consistent grade of coal before final acceptance. Under optimum conditions there will be no problems with sampling at isokinetic rates.

8- Permanganate vs. Gold Trains

Samples were collected using trains containing gold backed by permanganate, and permanganate backed by gold. The results of these studies are extracted from Table 3 and are presented in Table 5. During short sampling periods there were no significant differences observed with either the permanganate or the gold. There are some problems in comparing the data from the runs containing a mixed train since only an aliquot of the permanganate solution is analyzed and all of the gold is analyzed. The sampling period and flow rate cannot be optimized for using both recovery systems simultaneously. Sensitivity problems with the gold were observed during the high volume (290 liters) extended sampling period of the first run on March 28. This was expected with the present analytical procedure.

The results of the mixed trains and the permanganate and gold trains showed that the gold recovery is as efficient as the permanganate. Based on the assumption that the permanganate does recover essentially all the mercury when reduced by SO_2, it is concluded that the gold also recovers essentially all the mercury when a backup amalgamator is used. The gold

is not affected by high SO_2 concentrations and has been satisfactorily used to collect mercury in 6% SO_2.

Table 5. Results obtained from $KMnO_4$-Au and Au-$KMnO_4$ sampling trains

Date	Time	Position 1		Position 2		Total	Concentration
			µg		µg	µg	µg/l.
3/25/72	1:40	K	2.3	Au	-	2.3	0.024
	3:20	K	1.96	Au	-	1.96	0.021
	4:03	K	1.89	Au	0.078	1.97	0.022
	5:10	Au	1.9	K	0.22	2.12	0.028
	5:30	K	1.51	Au	-	1.51	0.022
	6:20	Au	1.1	K	0.21	1.3	0.018
3/27/72	12:15	K	2.59	Au	0.69	3.28	0.025
	1:18	Au	2.3	K	<0.5	<2.8	<0.023
	2:17	Au	4.7	K	0.4	5.1	0.027
	3:05	K	3.93	Au	0.59	4.52	0.024
	4:04	K	5.96	Au	0.08	6.35	0.025
	5:34	Au	4.68	K	0.65	5.33	0.022
3/28/72	9:53	Au	1.69	K	0.39	2.08	0.006
	10:49	K	4.43	Au	0.16	4.59	0.025
	1:17	K	2.50	Au	0.29	2.79	0.040
	2:00	Au	1.85	K	0.90	2.95	0.013
	2:43	Au	1.93	K	<0.3	1.93	0.014

9- Efficiency

The efficiency of recovery of volatile mercury by gold was investigated by interpreting the percent recovery of mercury on the first amalgamator where two amalgamators were used in series. The data is presented in Table 1. The gold was fired each night resulting in rejuvenated gold at the start of each day. Four amalgamators were prepared each day and were cycled through the runs using two during each sampling. Under optimum conditions, 90-98% recovery was obtained on the first amalgamator. The parameter most seriously

affecting the percent recovery was gold deterioration. Figure 22 contains the percent recoveries from two days runs as a function of the usage of the gold. The recovery of the efficiencies on April 19 is a result of rejuvenating the gold by firing at 750°C for 3½ hours between the runs. The relationships are not immediately obvious in each days run due to the effect of other parameters on the results and different procedures utilized in the treatment of the gold during various stages of the study.

10- Particulate Analyses

Particulate samples collected on April 13, at Site 1 and on April 19 and 20 at Site 2 were analyzed for mercury by the gold amalgamation flameless atomic absorption procedure identical to that used for the standards. The fiber glass filter samples collected in the standard EPA sampling train were digested by (1) perchloric acid-nitric acid digestion in a Bethge apparatus, and (2) volatilization of the mercury by combustion in an induction furnace accompanied by absorption of the volatilized mercury in a nitric-permanganate solution.

The perchloric acid digestion procedure consisted of adding 5 ml. of concentrated HNO_3 and 10 ml. of perchloric acid to the filter paper in a Bethge apparatus. Digestion was carried out by collecting the condensed volatiles until the solution reached 198°C and then refluxing for ten minutes. These samples were reduced with 5 ml. of the standard stannous chloride solution and analyzed by the same procedures as the standards.

The induction furnace procedure consisted of folding filter paper and

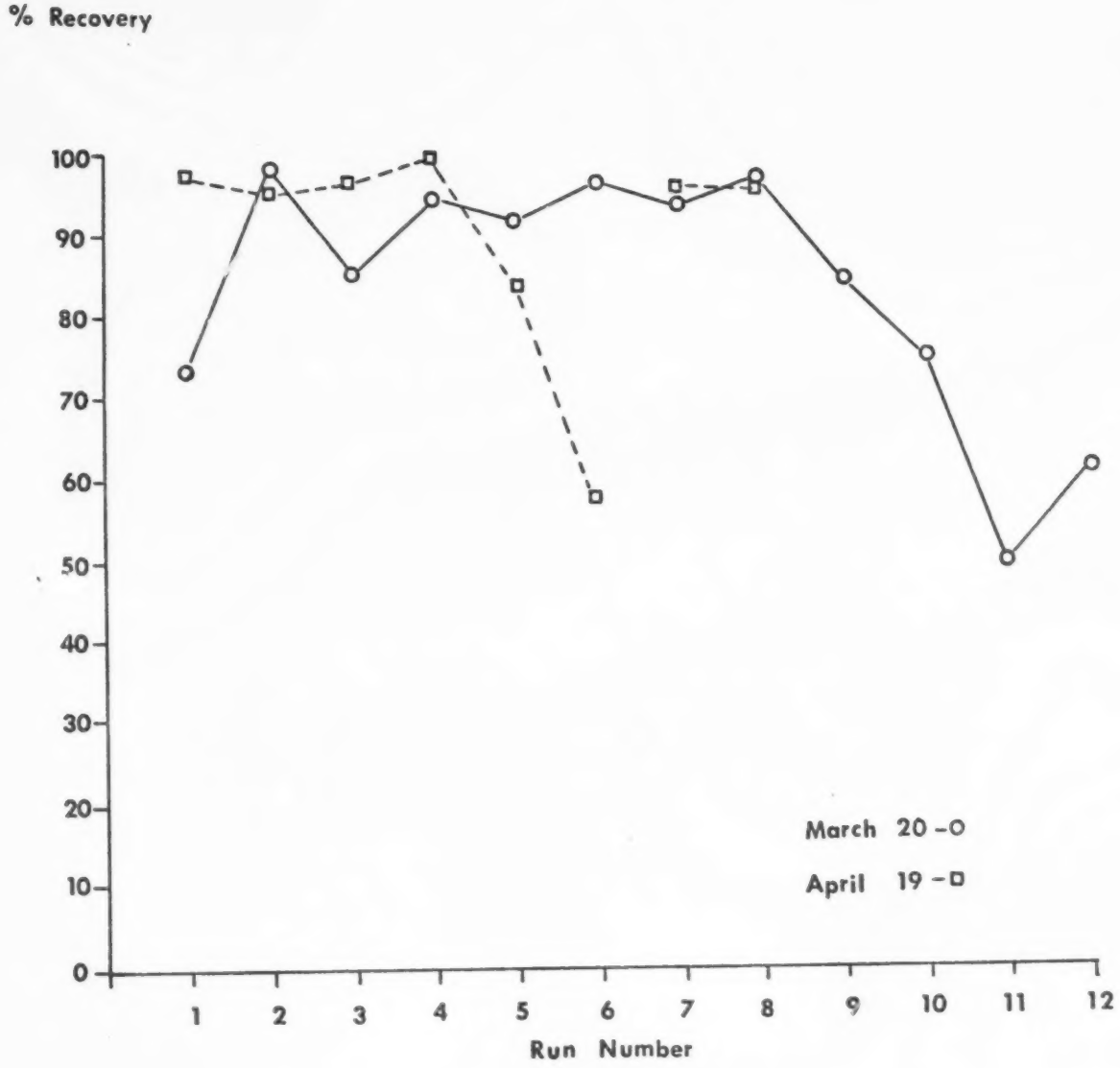


Figure 22. The Percent Recovery of Mercury on the First Amalgamator

placing it in the quartz-graphite crucible which was fired in the induction field at an 80% variac setting. An air stream carried the volatilized mercury through the bubbler illustrated in Figure 1 where the mercury was oxidized by an acidic permanganate solution (20 ml. saturated $KMnO_4$, 5 ml. conc. HNO_3, and 25 ml. distilled water) which removed the mercury from the air stream. The excess permanganate was reduced by adding 5 ml. of a 10% (W/V) hydroxylamine hydrochloride solution. The mercury was then reduced with 1 ml. of the standard stannous chloride solution and analyzed by the same procedure used for the standards and the perchloric acid digestions.

Because a whole filter paper was used for each analysis the reproducibility of the results could not be checked. Although similar results were obtained with the perchloric acid and induction furnace procedures, the induction furnace method was favored by the analysts. This preference was based on the inability to adequately control the reduction reaction. The results from the induction furnace procedure are in Table 6. The mercury concentrations are stated as a function of the gas volume because the weight of particulates collected during a 5 minute sampling period was too small to be measured accurately. The erratic results on April 13 are due to a fire in the coal bunker at the power plant resulting in very high particulate concentrations when the water soaked coal was burned. The results from April 19 and 20 illustrate the differences before and after an electrostatic precipitator.

Table 6. Particulate analyses by induction furnace-permanganate digestion

Date	Time	Mercury Concentration		Location
		µg/filter paper	µg/M^3	
April 13, 1972	10:55 A.M.	.07	.98	Cyclone Outlet
	11:30 A.M.	.03	.40	
	12:33 P.M.	.40	5.7	
	4:17 P.M.	.12	1.7	↓
April 19, 1972	9:30 P.M.	.075	.95	Precipitator Outlet
April 20, 1972	9:47 A.M.	.05	.35	
	10:33 A.M.	.075	.51	
	11:17 A.M.	.06	.68	
	12:04 P.M.	.06	.62	
	12:51 P.M.	.025	.60	
	2:16 P.M.	.09	.40	
	2:59 P.M.	.09	.86	
	3:39 P.M.	.03	.43	↓
	4:33 P.M.	.185	3.3	Precipitator Inlet
	5:13 P.M.	.119	1.4	↓

CONCLUSIONS

A method for collecting and analyzing mercury in power plant stack gases has been developed. The collection procedure consists of modifying a standard EPA isokinetic sampling train, utilizing two modified impingers containing 10 grams of gold chips to collect the mercury vapor as an amalgam. Particulates containing mercury are collected on a fiber glass filter upstream of the gold amalgam. The analytical procedure consists of transferring the modified impinger containing the mercury amalgam to an induction furnace. The induction field instantaneously volatilizes the mercury and an air stream carries it through a quartz optical cell positioned in the 254 mμ mercury line of an atomic absorption spectrophotometer. The mercury concentration is calculated from a peak obtained on the strip chart recording of the absorption pattern.

The sampling train utilizes two amalgamators in series as a method of verifying the efficiency of recovery of the first amalgamator. Under optimum conditions the percent recovery on the first amalgamator is about 95%. Gold deterioration and, possibly, stack turbulence will lower this recovery ratio. A very recent study by the U. S. Bureau of Mines[7] has also suggested that when the gold is warmed by the stack gas, small amounts of mercury are revolatilized by a flowing air stream and are carried to the second amalgamator. This would be in agreement with the observed results suggesting a higher recovery when the system is cooler.

The analytical procedure was found to be too sensitive resulting in a maximum sampling period of 5 to 10 minutes. Several methods of desensitizing the procedure have been suggested.

Although the procedure does require further refinement, accurate results are obtainable from stack gases at this time. Presently the authors are not able to differentiate between the range of the analytical values observed and the range of the results due to fluctuations in the coal consumption and the coal composition. The sampling and analytical procedure has been developed to the position where an accurate mercury concentration can be obtained within two days of on site sampling. The first day is spent in finding the range of the mercury concentration and the second day in obtaining the usable results. The procedure has not been sufficiently developed to permit shipping the samples back to the stationary laboratory for analyses after the sampling is completed.

FUTURE INVESTIGATIONS

Utilizing the procedure recommended in this study, gold amalgamation has been shown to be an efficient method of collecting several micrograms of volatile mercury under the SO_2 conditions observed in power plants. This investigation has shown the analytical procedure to be the limiting factor: the peak height cells are too sensitive and the integrating or flow through cell is too dependent on the exact amalgamation reaction prohibiting matching standards and samples. Immediate future work should be oriented toward either improving the present system or redesigning the system to permit a lower sensitivity.

Present System

(1) The present system may be improved by utilizing a large volume-short path length peak height cell. This cell will desensitize the system, but baffles may be required to approximate a homogeneous gas mixture.

(2) A gas mixing chamber between the amalgamator and the optical cell may provide a homogeneous enough mixture to permit using the present integrating cell or the large volume cell described in item 1 without baffles.

(3) Double amalgamation would permit amalgamating the standards and samples identically, theoretically permitting the use of any of the systems investigated. The procedure would consist of transferring

the gold from the impinger into another amalgamator tube, firing the amalgam, recollecting the mercury on another amalgamator above it, and then firing the second amalgamator carrying the volatilized mercury into the optical cell. The standard would then be aerated onto the first amalgamator, fired onto the second amalgamator and then fired into the optical cell. Both the standards and samples would be amalgamated onto the upper gold at the same flow rate and relative concentrations resulting in a similar release when the second amalgam is fired.

Modified System

(4) A cycling system would permit desensitizing the system by increasing the volume that the volatilized mercury is cycling through. The procedure would consist of volatilizing the mercury by firing the amalgamator and then, by the use of a one way valve and a pump, cycling the mercury through a closed loop containing the optical cell. Instead of a peak, a line would result which, after the gas had become homogeneous, would correspond to the mercury concentration. A method of desensitizing the system during cycling could be done by increasing the volume of the system with a large modified syringe. This unit would permit greater flexibility with an individual sample since one sample can be diluted during analyses if it has a high concentration.

Additional study of the following areas would result in a more efficient sampling and analytical procedure.

Analytical Method

1- The behavior of sulfuric acid mist, including the chemical breakdown of sulfuric acid during firing, should be more completely investigated.

2- Additional study of the behavior of the gold during amalgamation could result in a smaller quantity of gold being required and, possibly, a higher recovery efficiency on the first amalgamator.

3- The induction furnace combustion procedure for measuring mercury in the particulates appeared to work very well, but additional work should be performed at higher particulate concentrations (longer sampling period or higher particulate loading in the gas stream). This would permit obtaining splits of the filter paper for duplicate analyses.

4- The parameters investigated for sample storage and shipment should be expanded and more thoroughly studied.

5- The feasibility of incorporating the Laboratory Data Control mercury monitor into the analytical procedure should be investigated.

Sampling Train

1- A better support system for the gold in the amalgamator

should be developed.

2- The effect of the probe and the filter box temperatures should be investigated under controlled conditions in the laboratory.

3- Additional work is required to verify the need for and then optimize the scrubber solution in the sampling train.

In conjunction with the modification of the analytical procedure a better source facility containing a constant loading and a consistent fuel supply will be advantageous for additional studies.

APPENDIX I

MERCURY-GOLD AMALGAM SHIPPING CHARACTERISTICS

The adaptation of the procedure investigated in this study for routine monitoring of mercury in stack gases is dependent upon the capability of shipping the amalgam from the sampling point to the analytical facilities. To test the feasibility of shipping the amalgam under adverse conditions gold foil was amalgamated with known quantities of mercury and stored in an oven at 100°C for 16 hour periods. These amalgams were stored in either the original amalgamators or in porcelain crucibles. After the 16 hour period, the amalgamators were run directly by flameless atomic absorption followed by identical standards run on the same amalgamator. The samples stored in the crucibles were poured back into an amalgamator and analyzed followed by a standard.

Table 7 contains the peak heights of the samples and standards stored in the amalgamators. With the exception of two of the runs the results are within the present experimental error. The amalgams that were transferred into the crucibles showed considerable variation reflecting the redistribution of the amalgamated gold foil in the non-amalgamated foil. The peak heights were in between the same standards amalgamated from the top down and from the bottom up. These results verified the initial conclusion that the standards must be amalgamated onto the gold by a procedure closely approximating the stack sampling procedure.

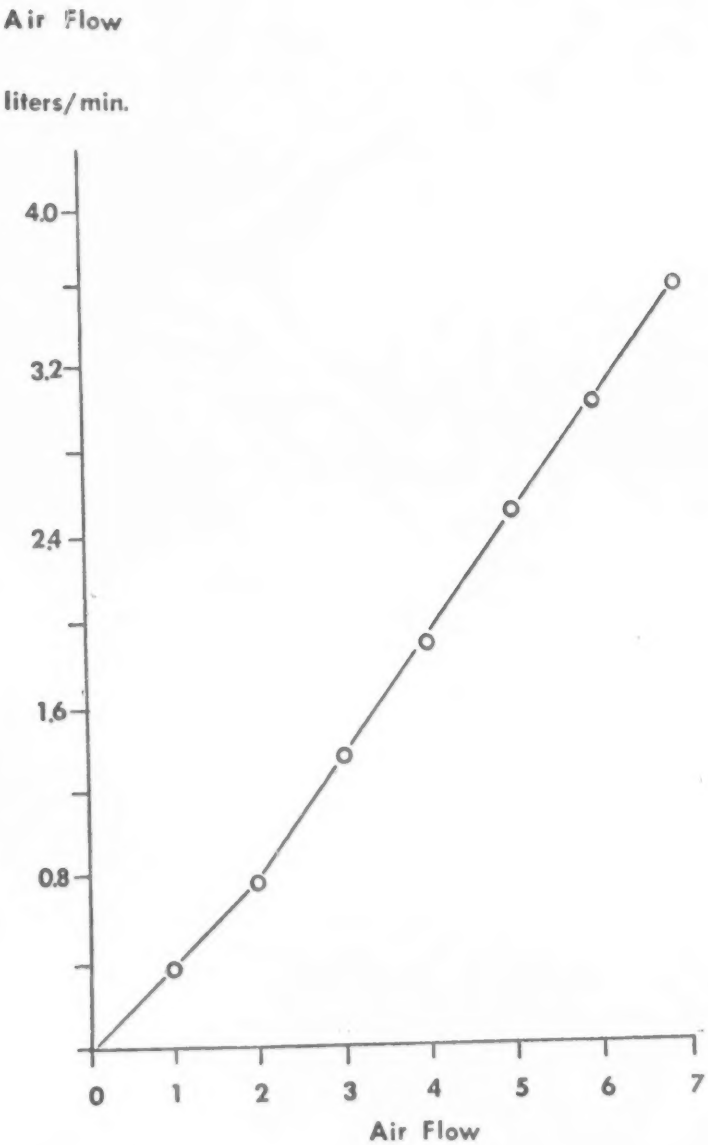
It is concluded from this limited study that under the conditions investigated

the amalgam is stable for extended periods of time. If the amalgam is to be transferred into another container for shipping a double amalgamation or cycling procedure will have to be adopted to account for the redistribution of the amalgam.

Table 7. Results of the effect of storing the amalgam at 100°C for 16 hours in the amalgamator.

	Percent Absorption	
	Sample	Standard
0.1µg	34.7	19
	33.5	26
0.2µg	39.8	38.9
	44.8	35
0.5µg	73.2	70.8
	54.4	60.2
1.0µg	85.5	86
2.0µg	89.5	82.5

APPENDIX II



Perkin Elmer Flowmeter

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